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16. ABSTRACT

The report describes the status of SO2 abatement technology for stationary sources in Japan as of June 1976. It presents the current status of desulfurization technologies including hydrodesulfurization of oil, decomposition of residual oil, gasification of coal and oil, and flue gas desulfurization (FGD). It examines the major Japanese FGD processes with respect to their applications, performance, economics, major technical problems, developmental status, byproducts, and raw materials. It also contains background information on energy usage, fuel resources, ambient concentration of pollutants, and emission regulations in Japan. It describes processes for the simultaneous removal of SOx and NOx from flue gases. It presents a comparative evaluation of flue gas cleaning technologies in the U.S. and Japan.

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| Sulfur Dioxide | Nitrogen Oxides | Stationary Sources | 07B | |
| Flue Gases | Energy | Japan | 21B | |
| Desulfurization | Regulations | Hydrodesulfurization | 07A,07D | 05D |
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# $SO_2$ ABATEMENT FOR STATIONARY SOURCES IN JAPAN

by

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## FOREWORD

This report describes the status in Japan of technology for desulfurization of flue gases and for simultaneous removal of sulfur dioxide and nitrogen oxides from flue gas streams. The information is current through May 1976. The total capacity for flue gas desulfurization in Japan has reached 70 million normal cubic meters per hour (23,000 megawatt equivalent) and is expected to exceed 100 million cubic meters per hour (33,000 megawatt equivalent) by the end of 1977.

Ambient concentrations of sulfur dioxide in Japan have decreased markedly as a result of the desulfurization efforts by industry and the increasing use of low-sulfur fuels. The need for control of nitrogen oxides, however, has increased; efforts are being concentrated, therefore, on developing technologies for the simultaneous control of both classes of pollutants.

Section 1 of the report describes fuel use patterns in Japan, ambient concentrations of pollutants, and the current emission regulations.

Section 2 reviews the status of hydrodesulfurization of heavy oil, asphalt decomposition, and coal gasification with emphasis on the new technology of asphalt decomposition to supply low-sulfur fuels.

Section 3 analyzes the status of flue gas desulfurization, including the major technical problems, trends, and economics.

Sections 4 and 5 describe in detail the applications of desulfurization technology by power companies and steel producers and the performance of new systems.

Sections 6 and 7 describe advanced processes for flue gas desulfurization and for simultaneous removal of the sulfur and nitrogen oxides.

Section 8 provides a comparative evaluation of advanced flue gas cleaning technologies in the United States and Japan.

# CONVERSION FACTORS & ABBREVIATIONS

The metric system is used in this report. Some of the conversion figures between the metric and English systems and abbreviations are shown below:

1 m (meter) = 3.3 feet

1 $m^3$ (cubic meter) = 35.3 cubic feet

1 t (metric ton) = 1.1 short tons

1 kg (kilogram) = 2.2. pounds

1 liter = 0.26 gallon

1 kl (kiloliter) = 6.29 barrels

The capacity of $SO_2$ and $NO_x$ removal plants is expressed in $Nm^3$/hr (normal cubic meters per hour).

1 $Nm^3$/hr = 0.59 standard cubic foot per minute

About 3,000 $Nm^3$/hr is equivalent to 1 megawatt.

L/G ratio (liquid/gas ratio) is expressed in liters/$Nm^3$.

1 liter/$Nm^3$ = 7.4 gallons/1,000 standard cubic feet.

For monetary conversions, the exchange rate of 1 dollar = 300 yen is used.

$SO_2$ and $NO_x$ removal costs are expressed in $/kl oil. $1/kl oil is equivalent to about 0.21 mil/kWh.

One liter heavy oil gives nearly 10,000 kcal (kilocalories).

1 kcal = 3.97 Btu.

Operability and availability, as referred to in the text, are defined as follows:

Operability (index): The number of hours the FGD system operated divided by the boiler operating hours in the period, expressed as a percentage.

Availability (index): The number of hours the FGD system was available for operation (whether operated or not) divided by hours in the period, expressed as a percentage.

## ABBREVIATIONS

| | |
|---|---|
| BPSD | Barrels per stream day |
| FGD | Flue gas desulfurization |
| HDS | Hydrodesulfurization |
| kW | Kilowatts |
| L/G | Liquid/gas ratio (see above) |
| MW | Megawatts |
| Nm$^3$/hr | Normal cubic meters per hour (see above) |

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## 1. FUEL USAGE AND REGULATIONS ON $SO_x$ AND $NO_x$

### SUPPLY AND USAGE OF ENERGY

The energy supply in Japan, after continuously growing at a yearly rate of more than 10 percent, has leveled off since 1974 because of economic depression caused by the international crisis in marketing of oil (Table 1-1). Supplies of imported oil, which accounts for more than 70 percent of Japan's total energy, decreased in 1974. Production of electric power in 1974 was slightly less than that in 1973, although the generating capacity increased (Tables 1-2 and 1-3).

Consumption of heavy oil, the major fuel in Japan, also decreased in 1974. Use of high-sulfur heavy oil (grade C) decreased markedly, whereas use of low-sulfur heavy oil (grade A) increased slightly (Table 1-4). Consumption of heavy oil by power companies also dropped, but use of sulfur-free fuels such as naphtha and LNG (liquefied natural gas) increased (Table 1-5). The average sulfur content of oils consumed by power companies decreased from 1.5 percent in 1970 to 0.54 percent in 1974. The price difference between low-sulfur and high-sulfur oils was about $30/kl in 1974 and $25/kl in 1976 (Table 1-6).

Table 1-1. SUPPLIES OF PRIMARY ENERGIES IN JAPAN[1]

| | 1970 | 1971 | 1972 | 1973 | 1974 |
|---|---|---|---|---|---|
| Hydroelectric power, $10^6$ MWhr | 80.0 | 86.8 | 87.9 | 71.6 | 84.8 |
| Atomic power, $10^6$ MWhr | 4.5 | 8.0 | 9.5 | 9.7 | 19.7 |
| Coal, $10^6$ t | | | | | |
| Domestic | 40.8 | 33.8 | 28.1 | 21.7 | 21.4 |
| Imported | 50.9 | 46.5 | 50.5 | 58.0 | 64.6 |
| Oil, $10^6$ kl | | | | | |
| Domestic | 0.9 | 0.9 | 0.8 | 0.8 | 0.8 |
| Imported | 234.1 | 248.7 | 275.7 | 318.6 | 305.8 |
| Natural gas, $10^9$ $m^3$ | 2.8 | 2.9 | 2.9 | 2.9 | 2.8 |
| LNG, $10^6$ t | 0.9 | 1.0 | 1.0 | 2.3 | 2.8 |
| Other, $10^{13}$ kcal | 1.0 | 1.4 | 1.2 | 0.6 | 1.0 |
| Total, $10^{13}$ kcal | 310.4 | 320.6 | 344.3 | 382.5 | 383.5 |

Table 1-2. POWER GENERATION CAPACITY

(1,000 MW)[1]

| | 1970 | 1971 | 1972 | 1973 | 1974 |
|---|---|---|---|---|---|
| Hydro | 20.0 | 20.1 | 20.7 | 22.6 | 23.5 |
| Thermal | 47.0 | 54.9 | 62.7 | 70.6 | 76.9 |
| Atomic | 1.3 | 1.3 | 1.8 | 2.3 | 3.9 |
| Total | 68.3 | 76.3 | 85.2 | 95.5 | 104.2 |

Table 1-3. POWER GENERATED[1]

($10^6$ MWhr)

| | 1970 | 1971 | 1972 | 1973 | 1974 |
|---|---|---|---|---|---|
| Hydroelectric | 80.1 | 86.8 | 87.9 | 71.6 | 84.8 |
| Thermal | 274.8 | 290.8 | 331.1 | 388.8 | 354.6 |
| Atomic | 4.6 | 8.0 | 9.5 | 9.7 | 19.7 |
| Total | 359.5 | 385.6 | 428.5 | 470.1 | 459.0 |

Table 1-4. DOMESTIC DEMAND FOR HEAVY OIL[1]

($10^6$ kl)

| | 1970 | 1971 | 1972 | 1973 | 1974 |
|---|---|---|---|---|---|
| Grade A (S=0.1-1.0) | 11.1 | 13.3 | 16.2 | 19.3 | 19.6 |
| Grade B (S=0.3-2.5) | 12.7 | 12.7 | 12.9 | 12.8 | 11.9 |
| Grade C (S=0.5-4.0) | 90.0 | 92.4 | 95.6 | 105.0 | 86.6 |
| Total | 113.8 | 118.4 | 124.7 | 137.1 | 118.1 |

Table 1-5. CONSUMPTION OF FUELS BY POWER COMPANIES[1]

| | 1970 | 1971 | 1972 | 1973 | 1974 |
|---|---|---|---|---|---|
| Coal, $10^6$ t | 18.8 | 13.9 | 10.7 | 8.3 | 7.3 |
| Heavy oil, $10^6$ kl | 34.5 | 35.3 | 38.1 | 42.8 | 34.7 |
| Crude oil, $10^6$ kl | 7.2 | 11.0 | 17.8 | 23.6 | 23.0 |
| Naphtha, $10^6$ kl | 0 | 0 | 0.2 | 2.2 | 3.5 |
| LNG, $10^6$ t | 0.7 | 0.7 | 0.6 | 1.4 | 2.5 |
| Natural gas, $10^6$ $Nm^3$ | 0.07 | 0.13 | 0.17 | 0.22 | 0.24 |
| Blast furnace and coke oven gases, $10^6$ $Nm^3$ | 15.6 | 18.1 | 22.9 | 32.4 | 32.4 |
| Average sulfur content, of oil, % | 1.50 | 1.31 | 1.03 | 1.75 | 0.54 |

Table 1-6. COST OF FUELS FOR POWER PLANTS

| Fuel | s, % | 1974 |  | 1976 |  |
|---|---|---|---|---|---|
|  |  | $/kl (t) | ¢/M Btu | $/kl (1) | ¢/M Btu |
| Naphtha | 0.02 |  |  | 110-115 | 245-255 |
| Crude oil | 0.3 | 86-90 | 210-220 | 96-100 | 234-244 |
| Heavy oil | 0.3 | 88-92 | 220-230 | 97-100 | 242-250 |
| Heavy oil | 1.6 | 72-75 | 180-188 | 80-84 | 200-210 |
| Heavy oil | 3.0 | 59-61 | 148-153 | 72-75 | 180-188 |
| Coal | 1-2.5 | (19-29) | 108-133 |  |  |

Domestic coal has been used for fuel. Although coal is cheaper than oil, as shown in Table 1-6, consumption will not increase because of the limited capacity of domestic coal mines. So far, all of the coal imported to Japan has been used for coke production for the steel industry. Importing of coal for fuel is expected to start in a year or two and to increase. In recent years, great efforts have been made to increase the imports of LNG because it causes no emissions of $SO_x$ and lower emissions of $NO_x$ than other fuels. Many contracts are under way with several countries (Table 1-7). There is considerable uncertainty with respect to the amount and the costs of LNG to be imported.

It is expected that the Japanese economy will recover by the end of 1976 and will gain strength slowly, with energy consumption increasing at a rate of 5 to 6 percent yearly (Table 1-8).

## EMISSION AND REGULATION OF $SO_x$

Japan today depends upon imported crude oil for more than 70 percent of its total energy supply. In 1974 and 1975, Japan imported nearly 300 million kiloliters of crude oil, which contained nearly 3 million tons of sulfur. Most of the sulfur in crude oil goes into heavy oil. More than 40 plants for hydrodesulfurization of heavy oil have been completed, and in 1975 about 30 percent of the oil was treated to produce 750,000 tons of elemental sulfur. Nearly

Table 1-7. PLANNED IMPORTS OF LIQUEFIED NATURAL GAS[1]

(LNG, 1,000 t)

| Source | Buyer | 1973 | 1975 | 1977 | 1979 | 1981 | 1983 | 1985 |
|---|---|---|---|---|---|---|---|---|
| Alaska | Tokyo Electric | 720 | 720 | 720 | 720 | 720 | 720 | 720 |
| | Tokyo Gas | 240 | 240 | 240 | 240 | 240 | 240 | 240 |
| Brunei | Tokyo Electric | 580 | 2,920 | 3,450 | 3,450 | 960 | 960 | 960 |
| | Tokyo Gas | 370 | 710 | 1,060 | 1,060 | 1,060 | 1,060 | 1,060 |
| | Osaka Gas | 350 | 500 | 630 | 630 | 630 | 630 | 630 |
| Abu Dhabi | Tokyo Electric | | | 2,800 | 2,800 | 2,800 | 2,800 | 2,800 |
| Indonesia | Kansai Electric | | | 100 | 1,490 | 2,400 | 2,400 | 2,400 |
| | Chubu Electric | | | 500 | 1,350 | 1,700 | 1,700 | 1,700 |
| | Kyushu Electric | | | 300 | 1,340 | 1,500 | 1,500 | 1,500 |
| | Osaka Gas | | | 380 | 1,140 | 1,300 | 1,300 | 1,300 |
| | Nippon Steel | | | 380 | 590 | 600 | 600 | 600 |
| Sarawak | Tokyo Electric | | | | | 4,000 | 4,000 | 4,000 |
| | Mitsubishi Shoji | | | | | 2,000 | 2,000 | 2,000 |
| Iran | | | | | | 2,500 | 2,500 | 2,500 |
| Other | | | | | | | 2,000 | 7,000 |
| Total | | 2,260 | 5,090 | 10,560 | 14,850 | 24,900 | 26,900 | 31,900 |

Table 1-8. LONG TERM ENERGY SUPPLY PLAN[1]

(MITI, August 1975)

| | 1973 | | 1980 | | 1985 | |
|---|---|---|---|---|---|---|
| | Amount | % | Amount | % | Amount | % |
| Domestic energy | | | | | | |
| Hydroelectric, $10^6$ MWhr | 71.6 | 4.6 | 85.5 | 4.2[a] | 100.3[a] | 3.7 |
| Geothermal, $10^6$ MWhr | 0.1 | 0.0 | 2.1 | 0.1 | 14.7 | 0.5 |
| Oil (gas), $10^6$ kl | 3.7 | 0.9 | 6.4 | 1.2 | 14.0 | 1.8 |
| Coal, $10^6$ t | 21.7 | 3.8 | 20.0 | 2.5 | 20.0 | 1.9 |
| Atomic power, $10^6$ MWhr | 9.7 | 0.6 | 95.4 | 4.4 | 278.3 | 9.6 |
| Imported energies | | | | | | |
| LNG, $10^6$ t | 2.4 | 0.8 | 20.6 | 5.2 | 42.0 | 7.9 |
| Coal (for coke), $10^6$ t | 58.0 | 11.7 | 87.3 | 12.7 | 87.8 | 9.6 |
| Coal (for fuel), $10^6$ t | 0 | 0 | 4.7 | 0.7 | 14.6 | 1.6 |
| Oil, $10^6$ kl | 318.0 | 77.4 | 393.0 | 68.9 | 485.0 | 63.3 |
| Total | | 100.0 | | 100.0 | | 100.0 |

[a] Including power to be generated by pumped storage power plants.

2 million tons of sulfur in heavy oil and crude oil was burned, constituting about 75 percent of the total emission of $SO_2$. About one-fourth of the heavy oil was burned in utility boilers of power companies and the rest by other industries. The ambient standard for $SO_x$ concentration was changed from 0.05 ppm (yearly average) to 0.04 ppm (daily average) in May 1973. By the new standard, the hourly average should not exceed 0.1 ppm and the daily average should not exceed 0.04 ppm. The standard is much more stringent than those in the U.S.A. and West Germany (Table 1-9). The values of K applicable to specific existing and new plant locations in Japan are provided in Table 1-10. The relation of K-values to maximum allowable ground-level $SO_2$ concentrations is presented in Table 1-11.

Table 1-9. AMBIENT AIR QUALITY STANDARDS

(Daily or yearly average, converted to ppm)

| | $SO_x$ | | $NO_2$ | |
|---|---|---|---|---|
| | Daily | Yearly | Daily | Yearly |
| Japan | 0.04 | 0.016 | 0.02 | 0.008 |
| United States | | 0.03 | 0.13 | 0.05 |
| West Germany | | 0.05 | | 0.05 |

The emission standard is given by the following equation:

$$Q = K \times 10^{-3} He_2$$

Q: Amount of sulfur oxides, $Nm^3/hr$ ($1\ Nm^3/hr = 0.59$ scfm).
K: The value shown in Table 1-10.
He: Effective height of stack, meters (1 meter = 3.3 ft).

## Table 1-10. VALUES OF K APPLICABLE TO LOCATIONS IN JAPAN

(For existing plants)

| K = 3.0 | K = 3.5 | K = 4.67 | K = 8.76 | K = 14.6 |
|---|---|---|---|---|
| Tokyo | Chiba | Sapporo | Hachinohe | Hakodate |
| Yokohama | Fuji | Kashima | Sendai | Miyako |
| Kawasaki | Handa | Shimizu | Niigata | Mobara |
| Yokkaichi | Himeji | Tokuyama | Okayama | Sasebo |
| Osaka | Mizushima | Omuta | Futuoka | Kagoshima |

(For new plants)

| K = 1.17 | K = 1.75 | K = 2.34 |
|---|---|---|
| Tokyo, Yokohama | Chiba, Fuji | Kashima, Omuta |
| Kawasaki, Nogoya | Kitakyushu | Ube, Oita |
| Yokkaichi, Osaka | Handa, Himeji | Shimizu, Kyoto |

## Table 1-11. RELATION OF K VALUE TO MAXIMUM GROUND-LEVEL CONCENTRATION OF $SO_2$

(ppm)

| K | 1.17 | 1.75 | 2.34 | 3.50 | 4.67 | 8.76 | 14.6 |
|---|---|---|---|---|---|---|---|
| $SO_2$ | 0.002 | 0.003 | 0.004 | 0.006 | 0.008 | 0.05 | 0.025 |

For a new plant with a capacity of 500 MW in the Tokyo and Osaka areas, the sulfur content of oil must be below 0.3 percent, even with a 200-meter stack. Through application of the regulations and such efforts as importing low-sulfur fuels, hydrodesulfurization of heavy oil, and flue gas desulfurization, ambient $SO_2$ concentrations in Japan have decreased, as shown in Figure 1-1.

## TOTAL MASS REGULATION OF $SO_x$

The emission standard has not succeeded in keeping the ambient concentration below 0.04 ppm daily average (0.016 ppm yearly average) in large cities and heavy industrial areas. With the aim of attaining the ambient standard by March 1978, the central government promulgated a new regulation in November 1974 to restrict the total mass of $SO_2$ emissions from the following eleven polluted areas: (1) Tokyo (2) Chiba (3) Yokohama, Kawasaki (4) Fuji (5) Nagoya (6) Handa (7) Yokkaichi (8) Osaka, Sakai (9) Kobe, Amagasaki (10) Kurashiki, Mizushima (11) Kitakyushu. The new regulation applies to plants using more than 0.1 to 1.0 kiloliter of oil per hour (0.4 to 4.0 MW equivalent; a certain number between 0.1 and 1.0 is to be assigned to each prefecture by the Governor). The amount of allowable $SO_x$ is calculated from one of the following formulas, to be selected by each prefecture:

$$Q = a \times W^b \qquad (1)$$

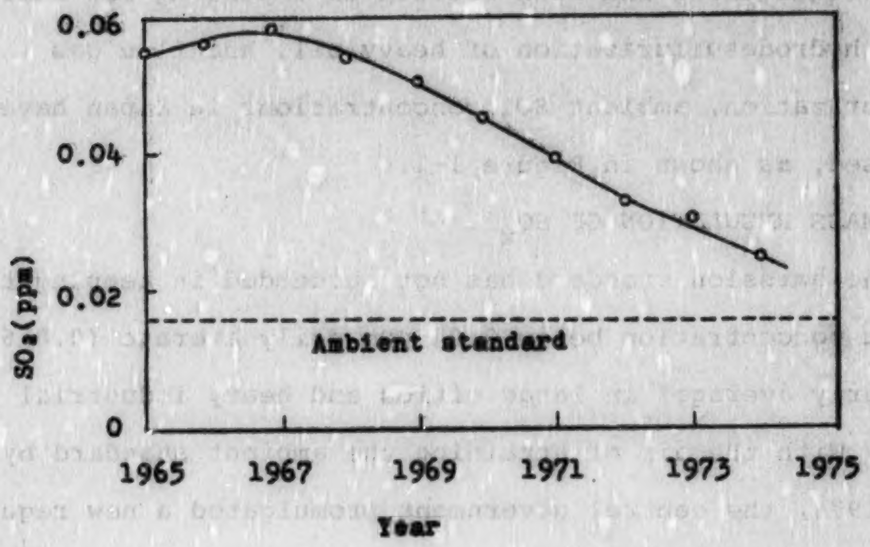

Figure 1-1. Yearly average $SO_2$ concentration in 15 major cities and industrial districts

Q: Amount of allowable $SO_x$
a: A constant to ensure $SO_x$ abatement
W: Amount of fuel used by each plant
b: A constant between 1.00 and 0.80 to be selected by the prefectural governor.

$$Q = Q_o \times C_m/C_{m_o} \qquad (2)$$

Q: Amount of allowable $SO_x$
$C_m$: Maximum ground level concentration to ensure $SO_x$ abatement
$C_{m_o}$: Maximum ground level concentration due to each plant
$Q_o$: Amount of $SO_x$ being emitted

Two prefectures, Mie (with Yokkaichi city) and Kanagawa (with Yokohama and Kawasaki cities), put the regulation in force recently. The regulations of Kanagawa are shown below.

$$Q = 1.5\ W^{0.865} + 0.5\ W_i^{0.865}\ \ldots\ldots\ldots\ (I)$$

$$Q = 2.5\ W^{0.865} + 0.8\ W_i^{0.865}\ \ldots\ldots\ldots\ (II)$$

Q: Amount of allowable $SO_x$, $Nm^3/hr$

W: Fuel consumption by existing plants, kl/hr

$W_i$: Fuel consumption by new plants, kl/hr

The equations are applied to plants that consume more than 1 kl oil per hour. Equation (I) is for most polluted districts in Yokohama and Kawasaki cities, and (II) is for other districts of the cities and for all parts of Yokosuka city. The allowable sulfur content of fuel oil, as calculated from the equations for different fuel consumptions, is shown in Table 1-12.

**Table 1-12. ALLOWABLE SULFUR CONTENT OF OIL - EXISTING AND NEW PLANTS**

(Percent)

| W | 1 | 10 | 100 | 1,000 |
|---|---|---|---|---|
| (MW equivalent) | (4.5) | (45) | (450) | (4,500) |
| Sulfur (I) | 0.238 | 1.174 | 0.124 | 0.094 |
| Sulfur (II) | 0.397 | 0.290 | 0.207 | 0.155 |
| $W_i$ | 1 | 10 | 100 | 1,000 |
| (MW equivalent) | (4.5) | (45) | (450) | (4,500) |
| Sulfur (I) | 0.079 | 0.058 | 0.041 | 0.031 |
| Sulfur (II) | 0.127 | 0.093 | 0.066 | 0.050 |

An existing 450-MW plant in district (I) is allowed to use oil with less than 0.124 percent sulfur. If the plant has two 225 MW units and one of them uses LNG with no sulfur, the other unit may use oil with 0.248 percent sulfur. New plants in district (I) need to use oil with less than 0.079 percent sulfur. Those plants will have to use naphtha, kerosene, or gas.

For plants consuming less than 1 kl/hr oil, sulfur content must be below 0.3 percent in district (I) and below 0.5 percent in district (II). The sulfur contents of fuel oils for diesel engine cars and ships are to be restricted to 0.2 and 0.5 percent, respectively. In districts other than (I) and (II), stationary sources are regulated by the national K-value control.

By those regulations, the total emission of $SO_x$ in districts (I) and (II), which was 5,348 $Nm^3/hr$ in 1973, will decrease to 2,078 $Nm^3/hr$ by the end of 1977; all districts in the Kanagawa prefecture will have an $SO_x$ concentration below the national environmental standard, 0.016 ppm yearly average (Figure 1-2).

## POLLUTION-RELATED HEALTH DAMAGE COMPENSATION LAW

One of the driving forces for progress in $SO_2$ abatement has been the "Pollution-Related Health Damage Compensation Law" which has been in effect since 1972. By the law, certain regions with prevalent pollution are designated as polluted areas, and certain inhabitants who are diagnosed by nominated doctors to have pollution-related sickness such as chronic bronchitis are designated as pollution-related patients. Firms which emit more than 5,000 $Nm^3/hr$ of flue gas in those regions must pay a tax according to the amount of $SO_2$; and tax is used to provide medical care for the patients.

The number of designated patients increased remarkably, as shown in Figure 1-3. Most of their illnesses are considered due to air pollution, mainly by $SO_2$. The total tax paid by the firms increased from $11 million in 1974 to $52 million in 1975; most of the tax was paid for $SO_2$ emissions. The tax rate, which changes each year, was 26¢/$Nm^3$ $SO_2$ in 1975. For example, a firm with a 100-MW boiler using 0.6

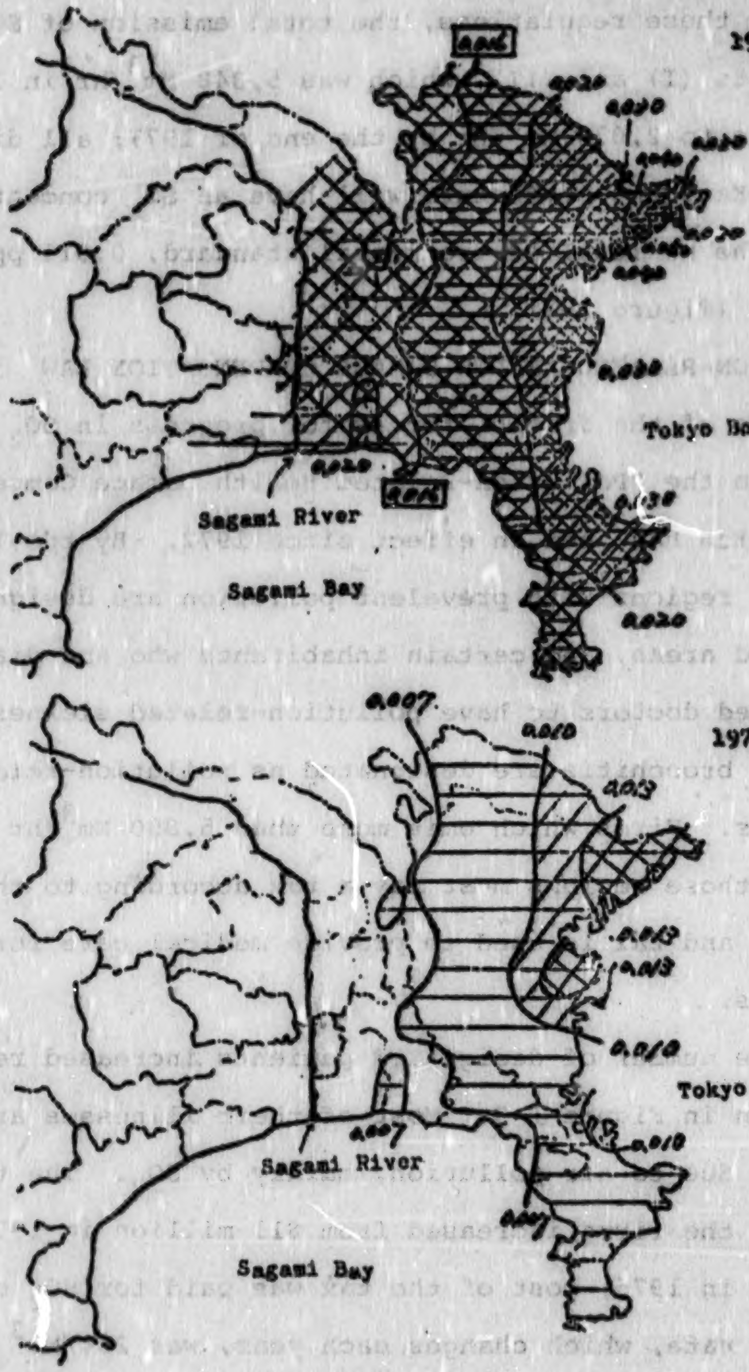
1973
0.016
0.020
0.030
0.040
0.030
0.020
Tokyo Bay
Sagami River
Sagami Bay
1977
0.007
0.010
0.013
0.013
0.013
0.010
0.007
0.010
0.007
Tokyo Bay
Sagami River
Sagami Bay

Figure 1-2. $SO_2$ concentration in Kanagwa prefecture (yearly average in 1973 and 1977, ppm).

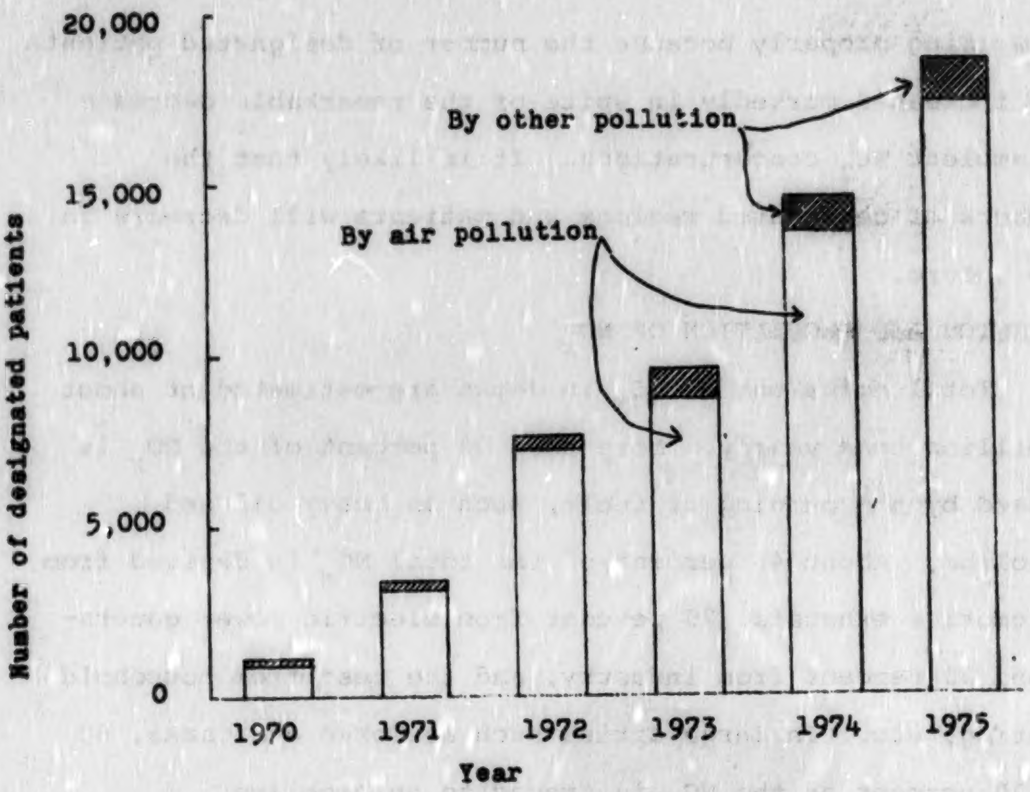

Figure 1-3. Increase of the designated patients.

percent sulfur oil paid about $160,000 in 1975. The tax is equivalent to about 1 percent of the cost of the fuel oil.

Several organizations now claim that the system may not be working properly because the number of designated patients has increased markedly in spite of the remarkable decrease in ambient $SO_2$ concentrations. It is likely that the numbers of designated regions and patients will decrease in the future.

## EMISSION AND REGULATION OF $NO_x$

Total emissions of $NO_x$ in Japan are estimated at about 2 million tons yearly. More than 90 percent of the $NO_x$ is caused by the burning of fuels, such as heavy oil and gasoline. About 40 percent of the total $NO_x$ is derived from automotive exhausts, 20 percent from electric power generation, 30 percent from industry, and the rest from household heating, etc. In large cities such as Tokyo and Osaka, 60 to 70 percent of the $NO_x$ is traced to automobiles.

The ambient air quality standard for $NO_2$ was set forth in 1973 at 0.02 ppm daily average, the most stringent standard in the world (Table 1-9). The present yearly average $NO_2$ concentration ranges from 0.02 to 0.03 ppm, and the daily average often reaches 0.04 to 0.07 ppm in many cities.

The $NO_x$ emission standard for stationary sources was first set up in 1973 and revised in 1975. Table 1-13 shows the standard for boilers larger than 100,000 $Nm^3$/hr. Similar figures have been assigned to smaller boilers between 10,000 and 100,000 $Nm^3$/hr since 1975. This standard also is more stringent than those in the U.S.A. and other countries.

Table 1-13. $NO_x$ EMISSION STANDARDS

(ppm)

| | For new boilers | | For existing boilers | |
|---|---|---|---|---|
| Fuel | 1973 | 1975 | 1973 | 1975 |
| Gas | 130 | 100 | 170 | 130 |
| Oil | 180 | 150 | 230 | 230 |
| Coal | 480 | 480 | 750 | 750 |

Even though combustion modifications and improvement of burners have been undertaken in efforts to meet the standard, the ambient air quality standard has not been attained, even with the stringent emission standard. More stringent regulations to restrict the total $NO_x$ emissions from stationary sources are to be applied in several prefectures. The new regulations will require construction of many flue gas denitrification plants, which remove more than 80 percent of the $NO_x$.

## 2. HYDRODESULFURIZATION AND DECOMPOSITION OF OIL AND GASIFICATION DESULFURIZATION

### STATUS OF HYDRODESULFURIZATION (HDS)

Eighteen heavy oil HDS systems have been constructed since 1967, as shown in Tables 2-1 and 2-2. HDS is accomplished by two methods. One is vacuum gas-oil HDS, by which the vacuum gas-oil obtained by vacuum distillation of heavy oil is desulfurized to about 0.2 percent sulfur. Although this treatment is relatively easy, it cannot desulfurize the residual oil from the distillation, which amounts to about 40 percent of the heavy oil and is rich in sulfur and metallic impurities. The second method is topped-crude HDS, by which heavy oil is treated directly. It is difficult to reduce sulfur content below 1 percent by this process. Since 1 percent sulfur oil has become unsatisfactory for use in many places, several oil companies, including Idemitsu Kosan, Seibu Oil, Asia Oil, and Maruzen Oil, have constructed new topped-crude HDS process plants to reduce sulfur to 0.3 percent or below by use of several reactors in series. Hydrogen consumption to decrease sulfur from 1.0 to 0.3 percent is about equal to that required to reduce it from 2.5 to 1.0 percent. About 700,000 tons of elemental sulfur

Table 2-1. HYDRODESULFURIZATION SYSTEMS BUILT BY 1971

| Refiner | Plant site | Process | Completed | Capacity, per day |  |
|---|---|---|---|---|---|
|  |  |  |  | Oil, BPSD | Sulfur, tons |
| Idemitsu Kosan | Chiba | UOP[a] | 1967 | 40,000 | 265 |
| Fuji Oil | Sodegaura | CRC | 1968 | 23,000 | 100 |
| Toa Nenryo | Wakayama | ER & E | 1968 | 25,000 | 180 |
| Daikyo Oil | Umaokoshi | Gulf | 1969 | 17,500 | 110 |
| Nippon Oil | Negishi | CRC | 1969 | 40,000 | 190 |
| Showa Oil | Kawasaki | Shell | 1969 | 16,000 | 66 |
| Kyushu Oil | Oita | Shell | 1969 | 14,000 | 55 |
| Mitsubishi Oil | Mizushima | UOP | 1969 | 30,000 | 100 |
| Maruzen Oil | Chiba | Union | 1969 | 35,000 | 165 |
| Seibu Oil | Yamaguchi | Shell | 1969 | 4,000 | 28 |
| Nippon Mining | Mizushima | Gulf[a] | 1970 | 27,760 | 165 |
| Koa Oil | Marifu | CRC | 1970 | 8,000 | 39 |
| General Oil | Sakai | ER & E | 1970 | 31,000 | 73 |
| Kashima Oil | Kashima | UOP[a] | 1970 | 45,000 | 265 |
| Daikyo Oil | Umaokoshi | Gulf | 1970 | 17,500 | 77 |
| Kansai Oil | Sakai | ER & E | 1971 | 20,000 | 88 |
| Koa Oil | Osaka | CRC | 1971 | 12,000 | 55 |
| Toa Nenryo | Kawasaki | ER & E | 1971 | 51,000 | 220 |
| Total |  |  |  | 465,260 | 2,241 |

[a] Topped-crude HDS processes; all others are for vacuum gas-oil HDS.

### Table 2-2. HYDRODESULFURIZATION SYSTEMS COMPLETED BETWEEN 1972 AND 1976

| Refiner | Plant site | Process | Year of completion | Capacity oil, BPSD |
|---|---|---|---|---|
| Nippon Oil | Negishi | CRC | 1972 | 28,000 |
| Idemitsu Kosan | Himeji | Gulf[a] | 1972 | 40,000 |
| Kyokuto Petroleum | Chiba | UOP | 1972 | 60,000 |
| Toa Nenryo | Kawasaki | ER & E | 1972 | 9,000 |
| Asia Kyoseki | Sakaide | CRC | 1972 | 15,000 |
| Kyushu Oil | Oita | UOP | 1972 | 25,000 |
| Showa Yokkaichi Oil | Yokkaichi | Shell | 1972 | 35,000 |
| Seibu Oil | Yamaguchi | Shell | 1972 | 1,000 |
| Nippon Oil | Muroran | CRC | 1973 | 40,000 |
| Toa Oil | Nagoya | CRC | 1973 | 30,000 |
| Nippon Mining | Mizushima | Gulf[a] | 1974 | 3,240 |
| Toa Oil | Nagoya | ER & E | 1974 | 37,000 |
| Kansai Oil | Sakai | ER & E | 1974 | 2,000 |
| Showa Yokkaichi Oil | Yokkaichi | Shell | 1974 | 5,000 |
| Mitsubishi Oil | Mizushima | UOP[a] | 1974 | 45,000 |
| Nippon Mining | Mizushima | UOP | 1975 | 60,000 |
| Idemitsu Kosan | Chiba | UOP | 1975 | 34,000 |
| Idemitsu Kosan | Tokuyama | UOP | 1975 | 45,000 |
| Idemitsu Kosan | Aichi | Gulf[b] | 1975 | 50,000 |
| Seibu Oil | Yamaguchi | Shell[b] | 1975 | 45,000 |
| Asia Oil | Yokohama | UOP[b] | 1975 | 30,000 |
| Asia Oil | Sakaide | Gulf[b] | 1976 | 28,000 |
| Toa Oil | Kawasaki | ER & E | 1976 | 46,000 |
| Fuji Oil | Sodegaura | CRC | 1976 | 35,000 |
| Maruzen Oil | Chiba | ER & E[b] | 1976 | 60,000 |
| Total | | | | 839,240 |

[a] Topped-crude HDS.

[b] New topped-crude HDS.

All others are for vacuum gas-oil HDS.

was recovered in 1973 by HDS; sulfur recovery has not increased much since then (Table 2-3), in spite of the completion of many new HDS plants. The slowdown in sulfur recovery was caused by economic depression; in 1975 operation of the HDS plants averaged only about 4,700 hours (54 percent of possible total of 8,760 hours).

About 25 HDS systems with a total capacity of nearly 1 million BPSD were planned for construction between 1976 and 1978. Most of the plans, however, were abandoned or postponed, partly because of the economic depression and partly because a great increase in the demand for heavy oil had become unlikely.

A rough estimate of HDS costs for heavy oil containing 3 percent sulfur at various desulfurization efficiencies is shown in Table 2-4, with FGD cost given for comparison. HDS is more expensive than FGD by the wet lime/limestone process but it is advantageous in that it produces elmental sulfur, which is a desirable by-product. The sulfur-by-producing FGD processes developed in Japan and other countries are more expensive, except for oil refineries that have Claus furnaces and hydrogen sulfide for sulfur production.

## RESIDUAL OIL DECOMPOSITION AND COAL GASIFICATION

### Outline

One of the major problems associated with HDS Technology is that its application is limited to heavy oil, containing

Table 2-3. AMOUNT OF SULFUR RECOVERED BY HDS AND FGD

(1,000 tons)

| | 1973 | 1974 | 1975 | 1976 |
|---|---|---|---|---|
| HDS | 700 | 720 | 750 | (800) |
| FGD[a] | 100 | 200 | 350 | (550) |

[a] Rough estimates including all sulfur compounds as converted into sulfur.

Table 2-4. APPROXIMATE COSTS FOR HDS AND FGD AT VARIOUS DESULFURIZATION EFFICIENCIES

($/kl, at 6,000 hours operation per year)

| Sulfur removal, % | 70 | 80 | 90 | 97 |
|---|---|---|---|---|
| Hydrodesulfurization | 16 | 19 | 23 | 27 |
| Flue gas desulfurization[a] | 16 | 17 | 18 | 19 |

[a] Wet lime/limestone process by-producing gypsum.

only small amounts of impurities because metallic impurities in the oil poison the HDS catalysts. It is estimated that only about 15 percent of the total heavy oil in Japan is suitable for the new topped-crude HDS process to reduce sulfur to 0.3 percent or below.

As demand for low-sulfur fuels increased, gasification desulfurization seemed promising in 1973, and many companies planned to construct gasification plants. Because of inflation following the oil crisis, however, most of the plans were given up. Ube Industries constructed a pilot plant to gasify 50 tons per day of heavy oil.[2] The Coal Research Center constructed a pilot plant to gasify 5 tons per day of coal. Activity at those works has been limited, however, by the economic situation.

Thermal decomposition of the vacuum residue of heavy oil (asphalt) with little gasification seems more promising. Two commercial plants have been constructed for this purpose. A plant with a capacity of treating 18,300 BPSD of asphalt was completed recently at Sodegaura Refinery, Fuji Oil, using the Eureka (Kureha) process. A plant capable of treating 50,000 BPSD of heavy oil is near completion at Kawasaki Refinery, Toa Oil, using the Flexicoking process.

Osaka Gas has developed a new process of asphalt decomposition and is operating a pilot plant.

## Eureka Process (Kureha Process)[4]

Kureha Chemical Industry has developed a new process to decompose the residue from vacuum distillation of heavy oil (asphalt) using steam to produce a cracked oil (about 65%), gas (about 5 wt %) and pitch (about 30%). A commercial plant owned by Eureka Industry Co. (established by Kureha Chemical jointly with Fuji Oil, Arabia Oil, and Sumitomo Metal) with a capacity of treating about 1 million tons of the residual oil yearly was completed in February 1976 at Sodegaura, Chiba Prefecture, and has been operating smoothly since March 1976 (Photo 2-1).

A flowsheet of the process is shown in Figure 2-1. The residual oil containing 4 to 5 percent sulfur is treated with steam heated to above 700°C in reactors at 500°C for several hours. The steam carries heat and promotes distillation.

Typical product patterns are shown in Table 2-5. The cracked naphtha and gas oil contain few heavy metal impurities and are easily treated by hydrodesulfurization. The gas from the reactor contains about 15 percent $H_2S$, which is removed by a conventional process using an amine. The purified gas (about 16,000 kcal/$m^3$) is used for fuel. The pitch, which contains 4 to 8 percent sulfur, is used by Sumitomo Metal as a binder for poor-coking coal in coke

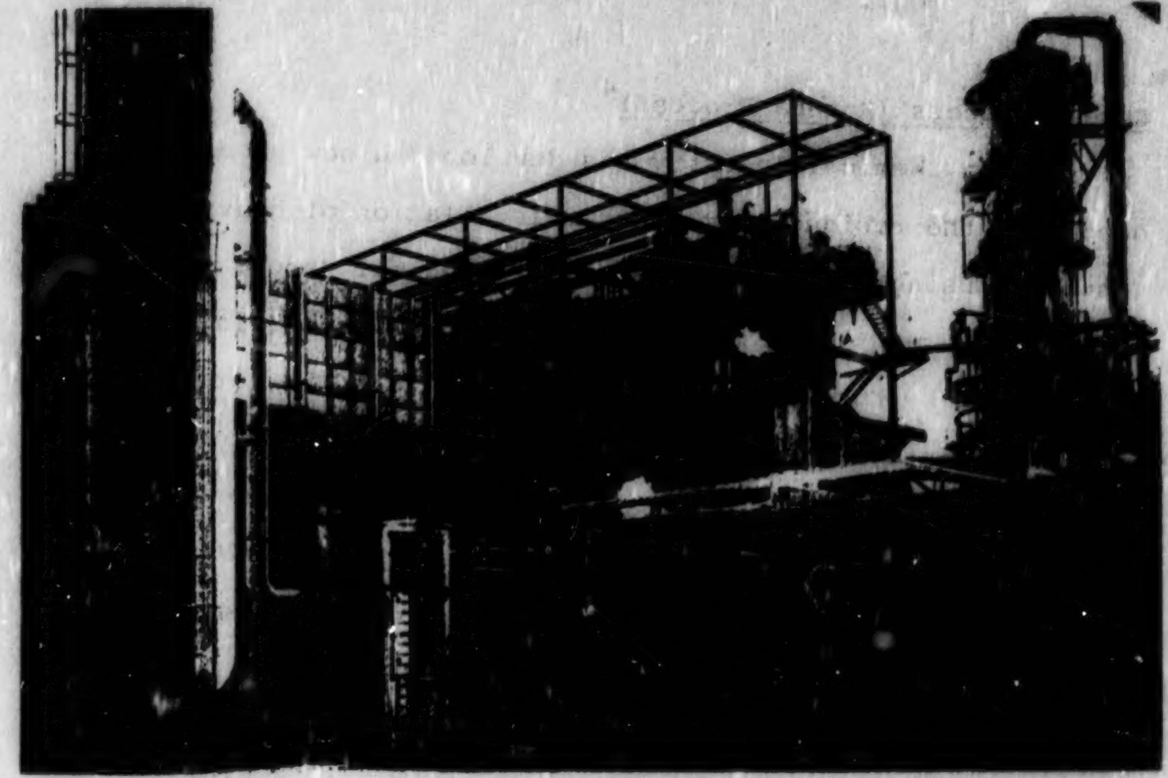

Photo 2-1. Sodegaura plant, Eureka.

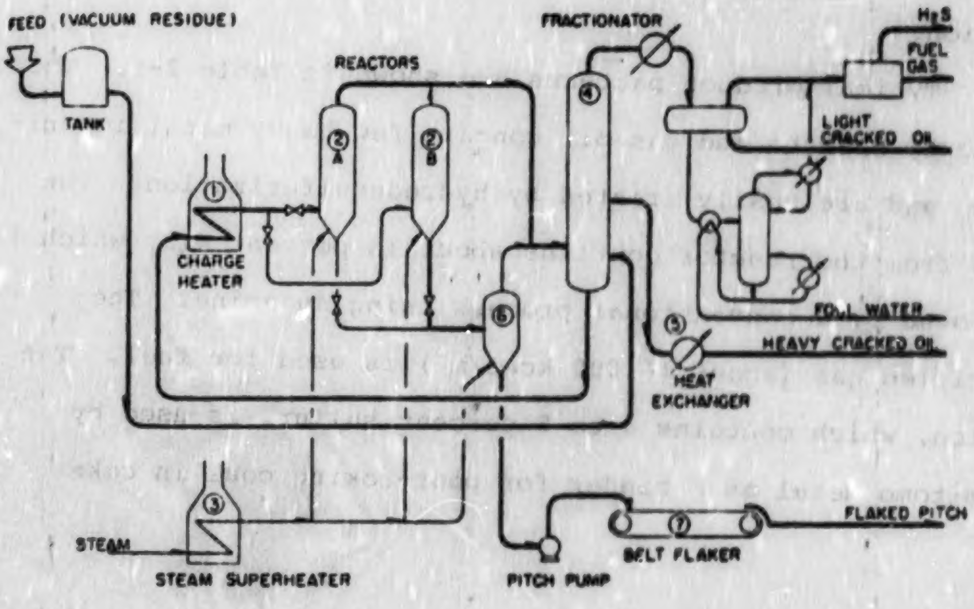
FEED (VACUUM RESIDUE)
TANK
REACTORS
②A
②B
①
CHARGE HEATER
FRACTIONATOR
④
$H_2S$
FUEL GAS
LIGHT CRACKED OIL
FOUL WATER
⑤
HEAT EXCHANGER
HEAVY CRACKED OIL
⑥
③
STEAM
STEAM SUPERHEATER
PITCH PUMP
⑦
BELT FLAKER
FLAKED PITCH

Figure 2-1. Flowsheet of Eureka process.

## Table 2-5. TYPICAL PRODUCT PATTERNS

(Values in percent by weight)

| Products | Khafji vacuum residue | | | Iranian Heavy vacuum residue | | |
|---|---|---|---|---|---|---|
| | Yield | Sulfur content | Sulfur distribution | Yield | Sulfur content | Sulfur distribution |
| Gas | 5.2 | 14.5 | 14.2 | 5.4 | 10.7 | 16.8 |
| Cracked naphtha | 8.3 | 1.9 | 3.0 | 11.3 | 1.7 | 5.6 |
| Cracked gas oil | 54.7 | 3.6 | 37.2 | 52.9 | 2.5 | 38.5 |
| Pitch | 31.8 | 7.6 | 45.6 | 30.4 | 4.4 | 39.1 |

NOTE: 1. Sulfur contents of Khafji vacuum residue and Iranian Heavy vacuum residue are 5.30 and 3.43 (% w), respectively.

2. Main components of gas are $C_1$-$C_5$ paraffins and olefins.

production. Kureha recently developed a process to produce a spherical activated carbon with the pitch.

The economic balance of the residual oil cracking process is shown in Table 2-6.

## Flexicoking

A commercial plant with a capacity of treating 50,000 bbl/day heavy oil by vacuum distillation and 21,000 bbl/day residual oil from the distillator (asphalt) by Flexicoking is under construction and scheduled to be completed by summer 1976 at Kawasaki refinery, Toa Oil. A rough material balance is shown in Figure 2-2. Vacuum gas oil from the distillator and gas oil from the Flexicoker will be treated by HDS (Gofiner). High-calorie gas will be sold to an adjacent steel producer, low-calorie gas will be consumed by Toa Oil, and the coke will be sold.

## Cherry Process

Osaka Gas Co., jointly with Mitsubishi Heavy Industries, has developed a new asphalt decomposition process to solve a common problem--coking on the reactor walls--by adding a small amount of pulverized coal to the asphalt. A pilot plant with a capacity of treating 26 t/day of asphalt was completed recently. A flowsheet is shown in Figure 2-3. Asphalt with a small amount of coal powder is heated to 400°C in a furnace, cracked and polymerized in a reactor,

Table 2-6. ECONOMIC BALANCE OF RESIDUAL OIL CRACKING PROCESS

(1 million tons of vacuum residue per year)

| | Unit price | | Cost | |
|---|---|---|---|---|
| | (yen/kg) | (¢/lb) | (million yen/year) | (million $/year) |
| Raw material | | | | |
| Vacuum residue, 1 million ton/yr | 13.2 | 2 | 13,200 | 44 |
| Processing cost | | | | |
| Utilities | | | 930 | 3.1 |
| Fixed cost (30% of investment) | | | 3,087 | 10.3 |
| | | | 17,217 | 57.4 |
| Products cost | | | | |
| Cracked oils 654 million ton/yr | 19.8 | 3 | 12,930 | 43.1 |
| Pitch 300 million ton/yr | 14.3 | 2.17 | 4,287 | 14.3 |
| | | | 17,217 | 57.4 |

NOTE: 1. Investment including off-site is 10,290 million yen in Japan, 1975.

2. The price of coal tar pitch is considered between 3¢/lb and 5¢/lb in Japan, 1975.

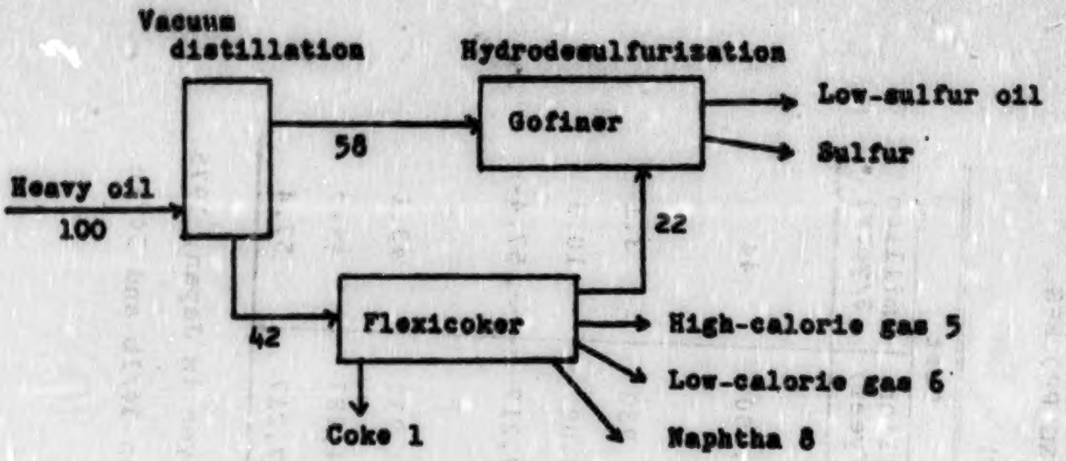
Vacuum distillation
Hydrodesulfurization
Gofiner
Low-sulfur oil
Sulfur
58
Heavy oil
100
22
Flexicoker
42
High-calorie gas 5
Low-calorie gas 6
Naphtha 8
Coke 1

Figure 2-2. Material balance for residual oil decomposition using Flexcoking process.

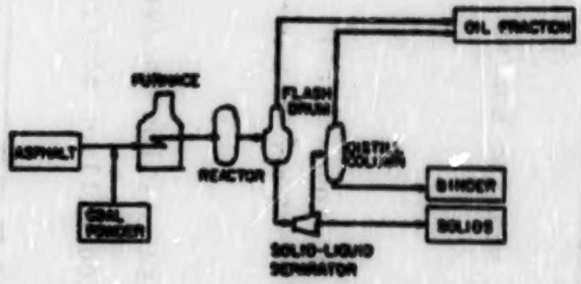
OIL FRACTION
FURNACE
FLASH DRUM
ASPHALT
REACTOR
DISTILL COLUMN
BINDER
COAL POWDER
SOLIDS
SOLID-LIQUID SEPARATOR

Figure 2-3. Flowsheet of Cherry Process.

then led into a flash drum, where lighter fractions are separated. The bottom product of the flash drum is centrifuged to separate liquids and solids. The liquid is sent to a distillation column to produce an oil and a pitch, which is used as a binder. The yield is 30 percent naphtha, 5 percent kerosene, 11 percent heavy fuel oil, 34 percent pitch binder, and 20 percent solids. The solid product is used as a coal substitute. A portion of the solids can be recycled to the system. No coking on the reactor walls has been observed.

### Coal Gasification

The Coal Research Center has continued tests on coal gasification with a 5-t/day pilot plant at Yubari, Hokkaido. Coal is gasified in a fluidized bed under 10 atmospheres pressure at 800 to 900°C with air and steam to produce a low-calorie gas (1,200 to 1,500 cal/$m^3$). A unit to desulfurize the gas by the Benfield process (a U.S. process) is under construction and is to start operation by the end of 1976. A plan to construct a 40-t/day test plant has been postponed.

Electric Power Development Co., which 2 years ago planned to construct a pilot plant for coal gasification, has postponed the plan and has joined the Coal Research Center in the development project.

## 3. GENERAL ASPECTS OF FLUE GAS DESULFURIZATION (FGD)

### TRENDS

Japan has made remarkable progress in flue gas desulfurization since 1972. About 100 systems, including several large ones with a capacity of 250 to 500 MW, went into operation in 1975. The total FGD capacity, which was about 40 million Nm$^3$/hr (13,000 MW equivalent) at the end of 1974, will exceed 80 million Nm$^3$/hr by the end of 1976. The rapid growth is due to the economic advantage of FGD over the use of low-sulfur fuels and to the reliability of process and operation. The growth rate may decline after 1977, however, for the following reasons:

(1) Ambient $SO_2$ concentrations in large cities and industrial districts have decreased to a range of 0.02 to 0.03 ppm, almost meeting the ambient standard.

(2) The recent economic depression has prevented industry from building new plants.

(3) Overproduction of FGD by-products and a decrease in the price difference between high-sulfur and low-sulfur oils (Table 1-6) have started an industry trend toward the use of low-sulfur fuels, because Japan has limited landspace available for discarding of useless by-products.

(4) The stringent $NO_x$ regulation is forcing industry toward flue gas desulfurization. Several processes for simultaneous removal of $NO_x$ and $SO_2$ have been developed, and industry is waiting for the new technology.

## MAJOR PROCESSES AND SYSTEMS

Table 3-1 lists major constructors of FGD units and numbers and capacities of the units to be operational by the end of 1977. The total number of the units will exceed 500 and the total capacity will reach 85,000,000 $Nm^3$/hr, which is equivalent to 28,000 MW. About 80 percent of the units are completed (as of April 1976). About half of the total capacity is for utility boilers (mostly oil-fired) and the rest for industrial boilers, iron-ore sintering machines, nonferrous metals plants, sulfuric acid plants, and similar operations.

About half of the total capacity uses the wet lime/limestone process to by-produce gypsum; 16 percent use the indirect lime/limestone process (double alkali type); 13 percent use regenerable processes to by-produce sulfuric acid, ammonium sulfate and elemental sulfur; and 24 percent use sodium scrubbing to by-produce sodium sulfite or sulfate. The average system capacities are 427,000 $Nm^3$/hr for wet lime/limestone, 291,000 $Nm^3$/hr for indirect lime/limestone, 378,000 $Nm^3$/hr for the regenerable processes, 59,600 $Nm^3$/hr for the sodium scrubbing processes. About 80 percent of the sodium scrubbing units by-produce sodium sulfite for paper mills, and the rest oxidize the sulfite by air bubbling to by-produce sulfate, which is either used in the glass industry or purged in wastewater.

A recent survey by the Heavy Industry Newspaper Co. has revealed that in addition to the 335 sodium scrubbing units listed in Table 3-1, there are nearly 500 small commercial sodium scrubbing systems with an average capacity of about 20,000 Nm$^3$/hr. The sodium scrubbing process is the least costly, and its operation is relatively easy.

## WET LIME/LIMESTONE PROCESS

### Outline

Wet lime/limestone process systems with a capacity larger than 60,000 Nm$^3$/hr (20 MW) are listed in Tables 3-2, 3-3, and 3-4. The first commercial system using a wet lime-gypsum process was constructed in 1964 by Mitsubishi Heavy Industries (MHI), licensed by Japan Engineering Consulting Co. to treat 62,500 Nm$^3$/hr of tail gas from a sulfuric acid plant, containing 2,200 ppm $SO_2$. Several problems, including scaling and corrosion, were encountered at the beginning of the operation. The problems have been gradually solved, and many FGD systems using wet lime/limestone processes have been constructed by MHI and other companies.

The MHI (or Mitsubishi-JECCO) process has been used most widely for oil-fired boilers, iron-ore sintering plants, etc., while the Chemico-Mitsui, Mitsui-Chemico, and Chemico-IHI processes have been applied to coal-fired boilers. Six other processes also have been used, mainly

## Table 3-1. NUMBERS AND CAPACITIES[a] OF FGD SYSTEMS EXPECTED TO BE OPERATIONAL BY END OF 1977

| Plant constructor | Wet lime limestone | | Indirect lime limestone | | Regenerable | | Sodium scrubbing | | Total | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mitsubishi Heavy Industries (MHI) | 33 | (18,270) | | | | | 3 | (292) | 36 | (18,562) |
| Ishikawajima H.I. (IHI) | 17 | (4,445) | | | | | 79 | (4,351) | 96 | (8,796) |
| Hitachi - Babcock | 13 | (6,940) | | | 2 | (590) | 15 | (603) | 30 | (8,133) |
| Mitsubishi Kakoki (MKK)-Wellman | 2 | (256) | | | 13 | (6,478) | 41 | (913) | 56 | (7,643) |
| Kawasaki Heavy Industries | 4 | (756) | 6 | (5,450) | | | 7 | (256) | 17 | (6,380) |
| Tsukishima Kikai (TSK) | 1 | (80) | 4 | (398) | 1 | (88) | 40 | (4,042) | 45 | (4,608) |
| Chiyoda Chemical Eng. and Const. | | | 14 | (4,459) | | | | | 14 | (4,459) |
| Oji Koei | | | | | | | 57 | (4,280) | 57 | (4,280) |
| Fuji Kasui Engineering | 7 | (3,954) | | | | | 6 | (270) | 13 | (4,224) |
| Kurabo Engineering | | | 5 | (413) | 1 | (18) | 106 | (3,751) | 112 | (4,182) |
| Mitsui Miike-Chemico | 4 | (2,744) | | | 1 | (500) | | | 5 | (3,244) |
| Ebara Manufacturing | | | 11 | (1,914) | | | 10 | (1,167) | 21 | (3,081) |
| Nippon Kokan (NKK) | 3 | (245) | 1 | (150) | 2 | (1,990) | 6 | (62) | 12 | (2,447) |
| Kureha Chemical | | | | | | | 8 | (1,431) | 8 | (1,431) |
| Showa Denko | | | | | | | 5 | (1,372) | 5 | (1,372) |
| Gadelius | | | | | | | 8 | (1,291) | 8 | (1,291) |
| Sumitomo (SCEC)-Wellman | | | | | 6 | (1,288) | | | 6 | (1,288) |
| Mitsui Metal Engineering | 4 | (1,006) | | | 2 | (130) | | | 6 | (1,136) |
| Kobe Steel | 5 | (1,125) | | | | | | | 5 | (1,125) |
| Japan Gasoline | 1 | (330) | | | 1 | (125) | | | 2 | (455) |
| Dowa Engineering | | | 4 | (423) | | | | | 4 | (423) |
| Niigata Iron Works | | | 1 | (185) | | | | | 1 | (185) |
| Mitsui Shipbuilding | | | | | | | 1 | (160) | 1 | (160) |
| Sumitomo Heavy Industries | | | | | 1 | (150) | | | 1 | (150) |
| Total | 94 | (40,181) | 46 | (13,392) | 30 | (11,357) | 335 | (19,961) | 505 | (84,891) |

[a] Number of units followed by total capacity in parentheses; capacities are in thousands $Nm^3/Hr$.

### Table 3-2. WET LIME/LIMESTONE PROCESS UNITS BY MHI PROCESS

(larger than 60,000 $Nm^3/hr$)

| User | Plant site | Capacity, 1,000 $Nm^3/hr$[a] | Source of gas | $SO_2$, ppm Inlet | $SO_2$, ppm Outlet | Absorbent | Year of completion |
|---|---|---|---|---|---|---|---|
| Nippon Kokan | Koyasu | 62.5 | $H_2SO_4$ plant | 2,200 | 200 | $Ca(OH)_2$ | 1964 |
| Kansai Electric | Amagasaki | 100 | Utility boiler[b] | 700 | 70 | $Ca(OH)_2$ | 1972 |
| Onahama Refining | Onahama | 92 | Copper smelter | 20,000 | 100 | $Ca(OH)_2$ | 1972 |
| Kawasaki Steel | Chiba | 120 | Sintering plant | 600 | 60 | $Ca(OH)_2$ | 1973 |
| Kansai Electric | Kainan | 400 | Utility boiler | 550 | 60 | $Ca(OH)_2$ | 1974 |
| Tokyo Electric | Yokosuka | 400 | Utility boiler | 250 | 40 | $CaCO_3$ | 1974 |
| Tohoku Electric | Hachinohe | 380 | Utility boiler | 850 | 85 | $Ca(OH)_2$ | 1974 |
| Kyushu Electric | Karita | 550 | Utility boiler | 800 | 75 | $Ca(OH)_2$ | 1974 |
| Kawasaki Steel | Mizushima | 750 | Sintering plant | 830 | 40 | $Ca(OH)_2$ | 1974 |
| Kansai Electric | Amagasaki | 375 | Utility boiler | 500 | 50 | $Ca(OH)_2$ | 1975 |
| Niigata Power | Niigata | 530 | Utility boiler | 700 | 70 | $Ca(OH)_2$ | 1975 |
| Kawasaki Steel | Mizushima | 900 | Sintering plant | 500 | 40 | $Ca(OH)_2$ | 1975 |
| Kawasaki Steel | Chiba | 320 | Sintering plant | 800 | 60 | $Ca(OH)_2$ | 1975 |
| Teijin | Ehime | 270 | Industrial boiler[b] | 1,700 | 60 | $Ca(OH)_2$ | 1975 |
| Mizushima Power | Mizushima | 611 | Utility boiler | 1,050 | 40 | $Ca(OH)_2$ | 1975 |
| Tohoku Electric | Niigata | 420 | Utility boiler | 550 | 55 | $CaCO_3$ | 1976 |
| Chubu Electric | Owase | 1,200 | Utility boiler | 1,500 | 35 | $Ca(OH)_2$ | 1976 (March) |
| Chubu Electric | Owase | 1,200 | Utility boiler | 1,500 | 35 | $Ca(OH)_2$ | 1976 (June) |
| Kawasaki Steel | Mizushima | 750 | Sintering plant | 550 | 40 | $Ca(OH)_2$ | 1976 |
| Toyobo | Iwakuni | 200 | Industrial boiler | 1,400 | 50 | $Ca(OH)_2$ | 1976 |
| Kashima Power | Kashima | 431 | Utility boiler | 1,000 | 100 | $CaCO_3$ | 1976 |
| Kyushu Electric | Karatsu | 730 | Utility boiler | 550 | 70 | $CaCO_3$ | 1976 |
| Kyushu Electric | Karatsu | 570 | Utility boiler | 550 | 70 | $CaCO_3$ | 1976 |
| Kyushu Electric | Ainoura | 730 | Utility boiler | 880 | 110 | $CaCO_3$ | 1976 |
| Kyushu Electric | Ainoura | 730 | Utility boiler | 880 | 110 | $CaCO_3$ | 1976 |
| Sakata Power | Sakata | 1,100 | Utility boiler | 950 | 50 | $CaCO_3$ | 1976 |
| Sakata Power | Sakata | 1,100 | Utility boiler | 950 | 50 | $CaCO_3$ | 1976 |
| Chugoku Electric | Shimonoseki | 1,200 | Utility boiler | 1,600 | 50 | $CaCO_3$ | 1976 |
| Confidential |  | 475 | Utility boiler | 500 | 65 | $Ca(OH)_2$ | 1976 |
| Confidential |  | 1,200 | Utility boiler | 550 | 65 | $Ca(OH)_2$ | 1976 |
| Confidential |  | 530 | Utility boiler |  |  | $CaCO_3$ | 1976 |

[a] 1,000 $Nm^3/hr$ = 590 scfm = 320 kW.

[b] All boilers are oil-fired.

Table 3-3. WET LIME/LIMESTONE PROCESS UNITS USING SCRUBBERS DEVELOPED IN THE UNITED STATES

(larger than 60,000 $Nm^3/hr$)

| User | Plant site | Capacity, 1,000 $Nm^3/hr$[a] | Source of gas | $SO_2$, ppm Inlet | $SO_2$, ppm Outlet | Absorbent | Year of completion |
|---|---|---|---|---|---|---|---|
| Babcock-Hitachi Process | | | | | | | |
| Chugoku Electric | Mizushima | 310 | Utility boiler | | | $CaCO_3$ | 1974 |
| Asahi Chemical | Mizushima | 481 | Industrial boiler | | | $CaCO_3$ | 1975 |
| Kansai Electric | Osaka | 500 | Utility boiler | | | $CaCO_3$ | 1975 |
| Chugoku Electric | Tamashima | 1,460 | Utility boiler | 1,500 | 60 | $CaCO_3$ | 1975 |
| Kansai Electric | Osaka | 500 | Utility boiler | | | $CaCO_3$ | 1975 |
| Chugoku Electric | Tamashima | 1,000 | Utility boiler | | | $CaCO_3$ | 1976 |
| Showa Power | Ichihara | 249 | Utility boiler | | | $CaCO_3$ | 1976 |
| Showa Power | Ichihara | 480 | Utility boiler | | | $CaCO_3$ | 1976 |
| Maruzumi Paper | Kawanoe | 342 | Industrial boiler | | | $CaCO_3$ | 1976 |
| Confidential | | 500 | Industrial boiler | | | $CaCO_3$ | 1976 |
| Electric Power Dev. | Takehara | 852 | Utility boiler[b] | | | $CaCO_3$ | 1977 |
| Ishikawajima Harima (IHI) - TCA Process | | | | | | | |
| Chichibu Cement | Kumagaya | 104 | Diesel engine | 700 | 50 | CaO | 1972 |
| Onahama Smeltery | Onahama | 120 | Converter | | | CaO | 1972 |
| Furukawa Mining | Ashio | 60 | $H_2SO_4$ plant | | | CaO | 1972 |
| Chichibu Cement | Kumagaya | 106 | Diesel engine | | | CaO | 1973 |
| Hibi Smeltery | Hibi | 300 | Smelter | | | CaO | 1974 |
| Tokuyama Soda | Tokuyama | 550 x 2 | Industrial boiler | | | | 1975 |
| Sumitomo Power | Niihama | 450 | Utility boiler | | | $CaCO_3$ | 1975 |
| Mitsui Alumina | Wakamatsu | 300 | Boiler, kiln | | | $CaCO_3$ | 1975 |
| Chemico - Mitsui and Mitsui - Chemical Processes | | | | | | | |
| Mitsui Aluminum | Omuta | 512 | Industrial boiler[b] | 2,000 | 200 | $Ca(OH)_2$[c] | 1972 |
| Mitsui Aluminum | Omuta | 552 | Industrial boiler | 1,500 | 150 | $CaCO_3$ | 1975 |
| Electric Power Dev. | Takasago | 840 | Utility boiler[b] | 1,500 | 150 | $CaCO_3$ | 1975 |
| Electric Power Dev. | Takasago | 840 | Utility boiler[b] | 1,500 | 150 | $CaCO_3$ | 1976 |
| Ishikawajima Harima (IHI) - Chemico Process | | | | | | | |
| Electric Power Dev. | Isogo | 900 x 2 | Utility boiler[b] | 500 | 70 | $CaCO_3$ | 1976 |

[a] 1,000 $Nm^3/hr$ = 590 scfm = 320 kW.

[b] Coal-fired boilers. Other boilers are oil-fired.

[c] Carbide sludge to by-produce throwaway calcium sulfite. Other plants by-produce gypsum.

## Table 3-4. WET LIME/LIMESTONE PROCESS UNITS USING OTHER PROCESSES

(larger than 60,000 $Nm^3/hr$)

| User | Plant site | Capacity 1,000 $Nm^3/hr^a$ | Source of gas | $SO_2$, ppm |  | Absorbent | Year of completion |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Inlet | Outlet |  |  |
| Fujikasui-Sumitomo process (Moretana scrubber) |  |  |  |  |  |  |  |
| Ide Paper | Fuji | 60 | Industrial boiler | 1,340 | 20 | $CaCO_3$ | 1974 |
| Sanyo Kokusaku Pulp | Onomichi | 140 | Recovery boiler | 4,000 | 40 | $CaCO_3$ | 1975 |
| Sumitomo Metal | Wakayama | 370 | Sintering machine | 650 | 20 | $CaCO_3$ | 1975 |
| Sumitomo Metal | Kokura | 92 | Heating furnace | 820 | 40 | $CaCO_3$ | 1975 |
| Sumitomo Metal | Kashima | 880 | Sintering machine | 650 | 30 | $CaCO_3$ | 1975 |
| Sumitomo Kainan Kokan | Wakayama | 182 | Heating furnace | 680 | 35 | $CaCO_3$ | 1975 |
| Sumitomo Metal | Kashima | 1,000 x 2 | Sintering furnace | 650 | 30 | $CaCO_3$ | 1976 |
| Sumitomo Metal | Kokura | 750 | Sintering furnace | 650 | 20 | $CaCO_3$ | 1976 |
| Nippon Kokan process (Spray tower absorber) |  |  |  |  |  |  |  |
| Nippon Sheet Glass | Yokkaichi | 120 | Glass furnace | 1,000 | 100 | $Ca(OH)_2$ | 1974 |
| Nippon Sheet Glass | Maizuru | 107 | Glass furnace | 1,550 | 200 | $CaCO_3$ | 1976 |
| Nippon Kokan | Fukuyama |  | Incinerator | 28,000 | 200 | CaO | 1976 |
| Kobe Steel process (Cal process) |  |  |  |  |  |  |  |
| Kobe Steel | Amagasaki | 175 x 2 | Sintering machine | 500 | 30 | $Ca(OH)_2$ | 1976 |
| Kobe Steel | Kobe | 350 | Sintering machine | 500 | 30 | $Ca(OH)_2$ | 1976 |
| Nakayama Steel | Osaka | 375 | Sintering machine | 500 | 30 | $Ca(OH)_2$ | 1976 |
| Chubu - MKK process (CM process) |  |  |  |  |  |  |  |
| Ishihara Chemical | Yokkaichi | 250 | Industrial boiler | 1,600 | 150 | $CaCO_3$ | 1974 |
| Mitsubishi Gas Chem. | Yokkaichi | 60 | Industrial boiler | 1,300 | 100 | $Ca(OH)_2$ | 1974 |
| Kawasaki Heavy Industry process |  |  |  |  |  |  |  |
| Jujo Paper | Akita | 84 | Recovery boiler |  |  | $CaCO_3$ | 1973 |
| Jujo Paper | Akita | 90 | Recovery boiler |  |  | $CaCO_3$ | 1975 |
| Unitika | Okazaki | 200 | Industrial boiler |  |  | CaO(MgO) | 1975 |
| Nippon Exlan | Saidaiji | 300 | Industrial boiler |  |  | $CaCO_3$(MgO) | 1975 |
| Nippon Steel process (SSD process) |  |  |  |  |  |  |  |
| Nippon Steel | Tobata | 200 | Sintering machine |  |  | Slag | 1974 |
| Nippon Steel | Wakamatsu | 1,000 | Sintering machine |  |  | Slag | 1976 |

[a] 1,000 $Nm^3/hr$ = 590 scfm = 320 kW.

for flue gas from oil-firing boilers, and three others for sintering plants.

Many of the plants constructed before 1974 use lime at a stoichiometry of 0.95 to 1.0 to remove 93 to 98 percent of the $SO_2$. Most of the plants constructed later use limestone ground to pass about 325-mesh screen at a stoichiometry of 1.0 to 1.05 to remove 90 to 96 percent of the $SO_2$. Virtually all of the plants by-produce salable gypsum.

A schematic flowsheet common to most processes, except the Chemico-Mitsui and Mitsui-Chemico processes which use no cooler (prescrubber), is shown in Figure 3-1. Flue gas passes through an electrostatic precipitator, a cooler, a scrubber, a mist eliminator, and a reheater, before being emitted from a stack. Types of scrubbers and examples of operation parameters are listed in Table 3-5. Calcium sulfite formed by the reaction of $SO_2$ with lime or limestone slurry is oxidized by air bubbles into gypsum, which is then centrifuged.

The Omuta plant of Mitsui Aluminum is the only plant that produces a throwaway calcium sulfite sludge on a large scale. The plant uses a two-stage Chemico venturi scrubber and a carbide sludge as the absorbent. The plant has been operated in an unsaturated mode; gypsum is not formed, although about 10 percent of the calcium sulfite is oxidized in the scrubber. Operation has been trouble-free since

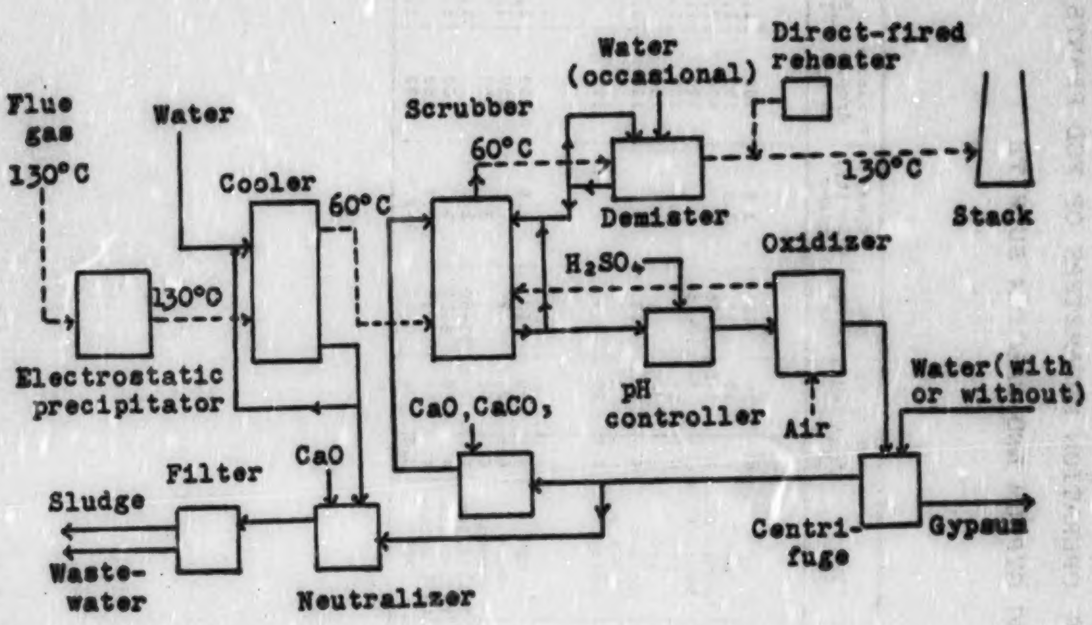
Flue gas
130°C
Water
Cooler
60°C
Scrubber
60°C
Water (occasional)
Direct-fired reheater
130°C
Stack
Demister
Oxidizer
$H_2SO_4$
130°C
Electrostatic precipitator
pH controller
Air
Water(with or without)
CaO,CaCO$_3$
CaO
Filter
Sludge
Waste-water
Neutralizer
Centri-fuge
Gypsum

Figure 3-1. Schematic flowsheet of wet lime/limestone gypsum process.

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## Table 3-5. EXAMPLE OF OPERATION PARAMETERS OF FGD PLANTS BY-PRODUCING GYPSUM AND CALCIUM SULFITE

| Process developer | Absorbent, precipitant (stoichiometry) | Capacity, 1,000 $Nm^3$/hr | Type of absorber | Slurry or solution, pH | Slurry or solution, conc.% | L/G, liter/$Nm^3$ | Space velocity, m/sec | Pressure drop,* mm $H_2O$ | $SO_2$, ppm In | $SO_2$, ppm Out | Moisture, % of gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wet lime-limestone process | | | | | | | | | | | |
| MHI (Mitsubishi-JECCO) | CaO 1 | 1,200[d] | GP[a] | 6.6 | 10 | 10 | 3.5 | 200 | 1,600 | 40 | 8-10 |
| MHI (Mitsubishi-JECCO) | $CaCO_3$ 1 | 750 | GP[a] | 6 | 10 | 10 | 3.5 | 150 | 1,000 | 80 | 8-10 |
| Chemico-Mitsui | $Ca(OH)_2$ 1-1.05 | 385 | venturi | 7 | 3-5 | 10-15 | | 400 | 2,000 | 150 | $CaSO_3$ |
| Mitsui-Chemico | $CaCO_3$ 1.0-1.05 | 840 | venturi | 6 | 5 | 10-15 | | 200 | 1,500 | 130 | 10-15 |
| Babcock-Hitachi | $CaCO_3$ 1.05-1.15 | 1,460[c] | PP[b] | 6.1 | 20 | 10 | 3.2 | 850 | 1,500 | 60 | 8-10 |
| Fuji Kasui-Sumitomo | $CaCO_3$ 1.05-1.15 | 800 | PP[b] | 6 | 5-6 | 5 | 4.5 | 200 | 500 | 20 | |
| Chubu-MKK | $CaCO_3$ | 250 | screen | 6 | 10 | 10 | 4 | 120 | 1,500 | 150 | 10-12 |
| Ishikawajima-TCA | CaO | 100 | TCA | | 2 | 7 | 3 | | 700 | 50 | 10-15 |
| Kobe Steel | CaO[f] 1.05 | 350 | spray | 6-8 | 30 | 3 | 3 | 190 | 300 | 20 | 10 |
| Indirect lime-limestone process | | | | | | | | | | | |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | 1,260[d] | GP[a] | 6.2 | 20 | 10 | 2.5 | 150 | 1,070 | 5 | 6-8 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | 500[c] | cone | 6.8 | 25 | 2 | | 250 | 1,400 | 40 | 8-10 |
| Nippon Kokan | $(NH_4)_2SO_3$, CaO | 150 | screen | 6 | 30 | 2 | 3 | 250 | 700 | 30 | 8-10 |
| Chiyoda | dil.$H_2SO_4$, $CaCO_3$ | 1,050 | Tellerette | 1 | 2-4 | 55-60 | 1 | | 1,600 | 60 | 7-9 |
| Kurabo | $(NH_4)_2SO_4$, CaO | 100 | Tellerette | 4 | 10 | 6-10 | 2 | 100 | 1,500 | 80 | 8-10 |
| Dowa | $Al_2(SO_4)_3$, $CaCO_3$ | 150 | Tellerette | 4 | 10 | 3[e] | 1.5 | 100 | 600 | 20 | 10-12 |
| Kureha | $CH_3COONa$, $CaCO_3$ | 5 | PP[b] | 5.5 | 20 | 7-8[g] | 2-2.5 | 280 | 1,400 | 1-3 | 6-7 |

[a] Grid packed.

[b] Perforated plate.

[c] Four scrubbers in parallel.

[d] Two scrubbers in parallel.

[e] For tail gas at 25°C. L/G 6-10 for flue gas.

[f] In $CaCl_2$ solution.

[g] Including limestone scrubbing.

* Including cooler, absorber, and mist eliminator.

start-up. For the recent FGD installations, Mitsui Aluminum selected a modified Mitsui-Chemico process to by-produce gypsum using limestone--because carbide sludge is getting short and the calcium sulfite sludge pond is becoming full.

### Scale Prevention

In many of the plants by-producing gypsum, more than 20 percent oxidation of calcium sulfite occurs, resulting in formation of gypsum in the scrubber. Gypsum crystals are usually recycled to the scrubber as seed crystals to eliminate the formation of gypsum on the surface of structural materials, which tends to cause scaling. Maintaining a smooth surface on the materials and a continuous flow of slurry in all parts of the scrubbers and pipings also aids in scale prevention.

Mist eliminators are most susceptible to scaling. Washing the eliminator with fresh water dissolves the scale but increases the volume of wastewater. A recent trend is to wash eliminators with circulating liquor and only occasionally with fresh water when some scale forms.

Scaling of the mist eliminator apparently is much more serious in the United States than in Japan. In the U.S.A. a large excess of limestone is often used to remove 80 to 90 percent of the $SO_2$. A mist containing a considerable amount of unreacted limestone adheres to the eliminator; passage of the gas containing 200 to 400 ppm of $SO_2$ and 2 to 4 percent

$O_2$ results in formation of gypsum on the mist eliminator. In Japan the excess of limestone is not so great, and the $SO_2$ concentration of the gas passing through the eliminator usually ranges from 20 to 150 ppm. Good reaction of limestone in the scrubber is attained by fine grinding and use of a higher L/G ratio.

## INDIRECT LIME/LIMESTONE PROCESS

### Outline

Processes developed to ensure scale-free stable operation, include double-alkali processes that use alkaline solutions for absorption and lime or limestone for precipitation, and also similar processes using acidic solutions for absorption. All of these processes are classified under the category of "indirect lime/limestone process." Operating parameters are shown in Table 3-5; major installations are listed in Table 3-6.

The scrubbing liquors are as follows: sodium sulfite for Kureha-Kawasaki, Showa Denko, and Tsukishima; ammonium sulfite for Nippon Kokan; dilute sulfuric acid containing ferric sulfate for Chiyoda; aluminum sulfate for Dowa; acidic ammonium sulfate for Kurabo; and sodium acetate for Kureha.

The pH values of the liquors are 6 to 7 for ammonium and sodium sulfites, 5 for sodium acetate, 3 to 4 for

# Table 3-6. INDIRECT LIME/LIMESTONE PROCESS INSTALLATIONS

| Process developer | Absorbent, precipitant | User | Plant site | Capacity, 1,000 Nm$^3$/hr | Source of gas | Inlet SO$_2$, ppm | Year of completion |
|---|---|---|---|---|---|---|---|
| Chiyoda | $H_2SO_4$, $CaCO_3$ | Nippon Mining | Mizushima | 34 | Claus furnace | 9,300 | 1972 |
| | | Fuji Kosan | Kainan | 160 | Industrial boiler | 770 | 1972 |
| | | Mitsubishi Rayon | Otake | 90 | Industrial boiler | 1,600 | 1972 |
| | | Daicel | Aboshi | 99 | Industrial boiler | 1,400 | 1973 |
| | | Tohoku Oil | Sendai | 14 | Claus furnace | 7,100 | 1973 |
| | | Mitsubishi Chem. | Yokkaichi | 420 | Industrial boiler | 1,200 | 1974 |
| | | Amagasaki Coke | Kakogawa | 36 | Incinerator | 11,300 | 1974 |
| | | Hokuriku Electric | | 750 | Utility boiler | 600 | 1974 |
| | | Mitsubishi Pet. | Yokkaichi | 150 | Industrial boiler | 1,300 | 1974 |
| | | Mitsubishi Pet. | Yokkaichi | 750 | Industrial boiler | 1,200 | 1974 |
| | | Gulf Power | Florida | 85 | Utility boiler | 1,700 | 1975 |
| | | Denki Kagaku | Chiba | 122 | Industrial boiler | 1,400 | 1975 |
| | | Hokuriku Electric | Fukui | 1,050 | Utility boiler | 1,500 | 1975 |
| | | Toyama Power | Toyama | 750 | Utility boiler | 1,500 | 1975 |
| Showa Denko | $Na_2SO_3$, $CaCO_3$ | Showa Denko | Chiba | 500 | Industrial boiler | 1,500 | 1973 |
| | | Kanegafuchi Chem. | Takasago | 300 | Industrial boiler | 1,500 | 1974 |
| | | Showa Pet. Chem. | Kawasaki | 200 | Industrial boiler | 1,400 | 1974 |
| Showa Denko-Ebara | $Na_2SO_3$, $CaCO_3$ | Nippon Mining | Saganoseki | 120 | $H_2SO_4$ plant | | 1973 |
| | | Yokohama Rubber | Hiratsuka | 105 | Industrial boiler | | 1974 |
| | | Nisshin Oil | Isogo | 100 | Industrial boiler | | 1974 |
| | | Poly Plastics | Fuji | 212 | Industrial boiler | | 1974 |
| | | Ajinomoto | Yokkaichi | 82 | Industrial boiler | | 1974 |
| | | Kyowa Pet. Chem. | Yokkaichi | 150 | Industrial boiler | | 1975 |
| | | Japan Food | Yokkaichi | 100 | Industrial boiler | | 1975 |
| | | Yokohama Rubber | Mie | 100 | Industrial boiler | | 1975 |
| | | Asia Oil | Yokohama | 243 | Industrial boiler | | 1975 |
| Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Tohoku Electric | Shinsendai | 420 | Utility boiler | 420 | 1974 |
| | | Shikoku Electric | Sakaide | 1,260 | Utility boiler | 1,500 | 1975 |
| | | Shikoku Electric | Anan | 1,260 | Utility boiler | 1,500 | 1975 |
| | | Kyushu Electric | Buzen | 730 | Utility boiler | 1,500 | 1977 |
| | | Tohoku Electric | Akita | 1,050 | Utility boiler | 1,500 | 1977 |
| Nippon Kokan | $(NH_4)_2SO_3$, $CaCO_3$ | Nippon Kokan | Keihin | 150 | Sintering plant | 400 | 1972 |
| Tsukishima | $Na_2SO_3$, CaO | Kinuura Utility | Nagoya | 185 | Industrial boiler | | 1974 |
| | | Daishowa Paper | Fuji | 264 | Industrial boiler | | 1975 |
| Kurabo Eng. | $(NH_4)_2SO_4$, CaO | Kuraray | Tamashima | 100 | Industrial boiler | 1,500 | 1974 |
| | | Daicel | Aboshi | 153 | Industrial boiler | 1,300 | 1975 |
| | | Bridgestone Tire | Tosu | 60 | Industrial boiler | | 1975 |
| | | Bridgestone Tire | Tochigi | 80 | Industrial boiler | | 1975 |
| | | Jujo Paper | Ishinomaki | 200 | Industrial boiler | 1,200 | 1976 |
| Dowa Mining | $Al_2(SO_4)_3$, $CaCO_3$ | Taenaka Mining | Mobara | 3,500 | Kiln | 7,500 | 1972 |
| | | Dowa Mining | Okayama | 300 | $H_2SO_4$ plant | 550 | 1974 |
| | | Naikai Engyo | Okayama | 70 | Utility boiler | 1,500 | 1975 |
| | | Yahagi Iron | Nagoya | 50 | Sintering plant | | 1976 |
| Kureha Chemical | $CH_3COONa$, $CaCO_3$ | Kureha Chem. | Nishiki | 5 | Utility boiler | 1,500 | 1975 |

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ammonium and aluminum sulfates, and 1 for sulfuric acid. The L/G ratios are 1/2 (7 to 14 gal/1,000 scf) for the solutions of pH 6 to 7, 3/10 for the solutions of pH 3 to 5, and 30/50 for the acid at pH 1. As acidity of the solution increases, the $SO_2$ absorption capacity and scaling are reduced and the reaction with limestone becomes easier. Limestone can be reacted with a sodium bisulfite solution, as in the Showa Denko and Kureha-Kawasaki processes, but the reaction occurs slowly and requires large reaction vessels. Lime is used for the Tsukishima, NKK, and Kurabo processes.

For the Chiyoda, Dowa, Kureha, and Kurabo processes, the liquors that absorb $SO_2$ are contacted with air to oxidize $SO_3^{--}$ into $SO_4^{--}$. Limestone or lime is then added to precipitate gypsum. For other processes, limestone or lime is added first to precipitate calcium sulfite, which is then oxidized into gypsum. In the double alkali type process, gypsum usually grows in larger crystals than in the wet lime-limestone process. Moisture content of the by-product gypsum after centrifugalization ranges from 6 to 12 percent as compared with 8 to 15 percent for the wet lime-limestone process.

The liquor from the gypsum centrifuge is returned mainly to the scrubber system. Softening of the liquor, which is usually needed to prevent scaling, is not required when pH of the acidic solution is below 5.

At most plants, a small portion of the liquor is purged to maintain the concentrations of chloride, magnesium, and other impurities under a certain level.

Sodium scrubbing provides high $SO_2$ recovery but involves sodium sulfate formation because of the oxidation of sodium sulfite. The sulfate must be decomposed because it does not absorb $SO_2$.

Compared with sodium scrubbing, ammonia scrubbing is less expensive because ammonia is cheaper than sodium hydroxide and ammonium sulfate is readily decomposed by lime. Plume formation is the major problem in ammonia scrubbing.

## Costs and Trends

Generally speaking, scale-free, stable operation is more easily attained by indirect lime/limestone processes than by the wet lime/limestone process, but the capital and operating costs are 5 to 10 percent higher (Table 3-9).

As successful operation of wet lime/limestone process units continues, the indirect processes are losing their advantage. Sodium-based indirect processes may be used, however, when more than 98 percent $SO_2$ removal is required, even though the processes are fairly expensive. Other indirect processes may be used at plants where the operation is not readily controlled to prevent scaling with a wet lime/limestone process.

## OTHER PROCESSES (RECOVERY PROCESSES)

### Sodium Sulfite By-production

There are 335 sodium scrubbing systems with an average capacity of treating 60,000 $Nm^3$/hr of flue gas (Table 3-1) and about 500 smaller units with an average capacity of 20,000 $Nm^3$/hr, by-producing mainly sodium sulfite, with some sulfate. As sodium hydroxide absorbs not only $SO_2$ but also $CO_2$, sodium sulfite is generally used to absorb $SO_2$ only. The product sodium bisulfite is neutralized with sodium hydroxide to produce the sulfite solution, half of which is returned to the scrubber and the rest to a concentration step. The by-product sulfite, in the form of either a concentrated solution or crystal, is sold to paper mills.

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$$

$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$

The process is simple and the system costs are low; demand for the sulfite, however, is limited. In several units the sulfite in solution is air-oxidized into sulfate, which is used for glass production, etc. From some smaller units, the sodium sulfite solution is purged. The number of sodium sulfite scrubbing systems will not increase significantly because of the oversupply of the by-products and the increase in cost of the sodium hydroxide.

## Wellman-Lord Process

Many Wellman-Lord process units have been constructed by Mitsubishi Kakoki Kaisha (MKK) and Sumitomo Chemical Engineering Co. (SCEC) (Table 3-7). The processes and the units were described in an earlier report.[2] Unit operation has been smooth. The major problem with the process has been treatment of wastewater to decompose reducing compounds. In addition to sodium thiosulfate $Na_2S_2O_3$, dithionate $Na_2S_4O_6$ is formed during heating of the sodium bisulfite solution, and the dithionate is not easily decomposed. MKK has succeeded in decomposing it by ozone oxidation at a pH below 1.5. The chemical oxygen demand (COD) is reduced enough to meet the regulation, but the treatment adds cost to the process. Most of the Wellman-Lord process units by-produce sulfuric acid; three units of oil companies by-produce elemental sulfur by feeding the recovered $SO_2$ into a Claus furnace.

## Magnesium and Zinc Scrubbing

There are two magnesium scrubbing units in operation (Table 3-7). Onahama plant, Onahama Smelting Co., sends the recovered $SO_2$ to a sulfuric acid plant, as reported earlier.[2,3] Chiba plant, Idenitsu Kosan, using the Chemico-Mitsui process, started operation recently, as described in Section 6.

Table 3-7. FGD INSTALLATIONS BY-PRODUCING $H_2SO_4$, S AND $(NH_4)_2SO_4$

| Process developer | Absorbent | User | Plant site | 1,000 $Nm^3/hr^a$ | Source of gas | Inlet $SO_2$, ppm | Year of completion | By-product |
|---|---|---|---|---|---|---|---|---|
| Wellman-MKK | $Na_2SO_3$ | Japan S.R. | Chiba | 200 | Industrial boiler | 2,000 | 1971 | $H_2SO_4$ |
| | | Chubu Electric | Nishinagoya | 620 | Utility boiler | 1,600 | 1973 | $H_2SO_4$ |
| | | Kashima Oil | Kashima | 30 | Claus furnace | 11,000 | 1973 | S |
| | | Japan S.R. | Yokkaichi | 450 | Industrial boiler | 1,000 | 1973 | $H_2SO_4$ |
| | | Toyo Rayon | Nagoya | 330 | Industrial boiler | 1,500 | 1974 | $H_2SO_4$ |
| | | J.N. Railways | Kawasaki | 700 | Industrial boiler | 1,500 | 1975 | $H_2SO_4$ |
| | | Mitsubishi Chem. | Mizushima | 628 | Industrial boiler | 1,500 | 1975 | $H_2SO_4$ |
| | | Kuraray | Okayama | 410 | Industrial boiler | 1,500 | 1975 | $H_2SO_4$ |
| | | Shindaikyowa Oil | Yokkaichi | 400 | Industrial boiler | 1,500 | 1975 | $H_2SO_4$ |
| | | Mitsubishi Chem. | Mizushima | 628 | Industrial boiler | 1,500 | 1976 | $H_2SO_4$ |
| | | Mitsubishi Chem. | Kurosaki | 530 | Industrial boiler | 1,500 | 1976 | $H_2SO_4$ |
| | | Tohoku Electric | Niigata | 380 | Utility boiler | 1,000 | 1977 | $H_2SO_4$ |
| Wellman-SCEC | $Na_2SO_3$ | Toa Nenryo | Kawasaki | 67 | Claus furnace | 6,500 | 1971 | S |
| | | Sumitomo Chem. | Sodegaura | 360 | Industrial boiler | 1,550 | 1973 | $H_2SO_4$ |
| | | Toa Nenryo | Wakayama | 17 | Claus furnace | 19,000 | 1974 | S |
| | | Fuji Film | Fujinomiya | 150 | Industrial boiler | 1,300 | 1974 | $SO_2$ |
| | | Sumitomo Chem. | Niihama | 155 | Industrial boiler | 1,600 | 1975 | $H_2SO_4$ |
| | | Sumitomo Chem. | Sodegaura | 540 | Industrial boiler | 1,600 | 1975 | $H_2SO_4$ |
| Onahama-Tsukishima | MgO | Onahama Smelting | Onahama | 84 | Copper smelter | 20,000 | 1972 | $H_2SO_4$ |
| Chimico-Mitsui | MgO | Idemitsu Kosan | Chiba | 500 | Claus and boiler | | 1975 | S |
| Mitsui Mining | MgO | Mitsui Mining | Hibi | 80 | $H_2SO_4$ plant | | 1971 | $H_2SO_4$ |
| | ZnO | Mitsui Mining | Kamioka | 50 | $H_2SO_4$ plant | | 1975 | $H_2SO_4$ |
| Shell | CuO | Showa Y.S. | Yokkaichi | 120 | Industrial boiler | 1,500 | 1973 | S |
| Sumitomo H.I. | Carbon | Kansai Electric | Sakai | 160 | Utility boiler | | 1971 | $H_2SO_4$ |
| Hitachi Ltd. | Carbon | Tokyo Electric | Kashima | 420 | Utility boiler | | 1972 | $H_2SO_4$ |
| | Carbon | Unitika | Oji | 171 | Industrial boiler | 1,500 | 1975 | $H_2SO_4$ |
| Nippon Kokan | $(NH_4)_2SO_3$ | Nippon Kokan | Fukuyama | 760 | Sintering plant | 400 | 1976 | $(NH_4)_2SO_4$ |
| | $(NH_4)_2SO_3$ | Nippon Kokan | Ogishima | 1,140 | Sintering plant | 400 | 1977 | $(NH_4)_2SO_4$ |
| Kurabo Engineering | $(NH_4)_2SO_4$ | Taki Chemical | Befu | 15 | Industrial boiler | 1,500 | 1976 | $(NH_4)_2SO_4$ |
| MHI-IFP | $(NH_4)_2SO_3$ | Maruzen Oil | Shimozu | 42 | Claus furnace | | 1974 | S |
| TEC-IFP | $(NH_4)_2SO_3$ | Fuji Oil | Chiba | 6 | Claus furnace | | 1974 | S |

[a] 1,000 $Nm^3/hr$ = 590 scfm = 320 MW.

Operation of a magnesium scrubbing system (80,000 $Nm^3/hr$) at Hibi Works, Mitsui Mining[2] was discontinued. A lime scrubbing system of larger capacity (300,000 $Nm^3/hr$) was constructed to replace it and is now in operation.

Kamioka plant, Mitsui Mining, started operation in 1975 to recover $SO_2$ from tail gas (50,000 $Nm^3/hr$) in a sulfuric acid plant by zinc oxide scrubbing. Zinc sulfite formed by the reaction is calcined to regenerate zinc oxide and $SO_2$; the latter is returned to the sulfuric acid plant. The process is similar to the magnesium scrubbing process. Although the calcination temperature is much lower with zinc (about 350°C) than with magnesia (about 950°C), zinc is expensive and entails some environmental hazards.

## Activated Carbon Process

Tokyo Electric Power operates an activated carbon process plant at Kashima (420,000 $Nm^3/hr$).[2] The $SO_2$ absorbed on carbon is washed with water to produce a weak sulfuric acid, which is treated with limestone to produce good-quality gypsum. The system has been operated without trouble for over 2 years. Virtually no carbon has been lost during the period.

Unitika Co. recently constructed a carbon process system to by-produce a stronger sulfuric acid (Section 6).

Operation continues at the dry carbon process plant of Kansai Electric at Sakai, using a moving bed designed by

Sumitomo Heavy Industry (formerly Sumitomo Shipbuilding).[2] After $SO_2$ absorption, the carbon is heated in a reducing gas to recover a concentrated $SO_2$ gas, which is used for sulfuric acid production. Consumption of the carbon is fairly high and there is no plan to construct a new system with the process. Sumitomo has been testing simultaneous removal of $SO_2$ and $NO_x$ in the process using ammonia (Section 7).

Ammonia Scrubbing

Nippon Kokan has developed a process to by-produce ammonium sulfate from $SO_2$ in flue gas and ammonia in coke oven gas[2] and is constructing two commercial plants (Table 3-7). To reduce formation of plume from the scrubber, which is a common problem with ammonia scrubbing processes, Nippon Kokan will use an afterburner to raise the temperature of the treated gas at its Fukuyama plant and a wet electrostatic precipitator at its Ogishima plant.

A small commercial plant to by-produce ammonium sulfate was completed recently by Kurabo Engineering for a fertilizer producer (Table 3-7, and Section 6).

Two relatively small units, with ammonia scrubbing, thermal decomposition of ammonium sulfate, and an IFP reactor to by-produce elemental sulfur, were constructed by Mitsubishi Heavy Industries and Toyo Engineering. Both have had problems, mainly in the decomposition step.

### Shell Process

The SYS system using the Shell copper oxide process has continued operation (Table 3-7). Tests have been performed for simultaneous removal of $NO_x$ by ammonia injection (Section 7).

### BY-PRODUCTS OF FGD

Desulfurization efforts in Japan are oriented toward processes that yield salable by-products (Figures 3-2 and 3-3). The reasons are that domestic supplies of sulfur and its compounds are limited in Japan, as is land for disposal of useless by-products. About 60 percent of the $SO_2$ is converted into salable gypsum, 20 percent into sodium sulfite, 15 percent into sulfuric acid, and the rest into waste calcium sulfite and sodium and ammonium sulfates.

The process that first became popular is sodium scrubbing to by-produce sodium sulfite for paper mills. Although this is the easiest FGD process, by-production of sodium sulfite will not increase greatly because the supply has filled the demand and because sodium hydroxide has become expensive.

The by-product gypsum can be grown into fairly large crystals useful for wallboard production and as a retarder of cement setting (Figure 3-4, Photo 3-1). Although the demand for gypsum decreased last year because of the economic depression, gypsum will continue to be the major by-product of FGD.

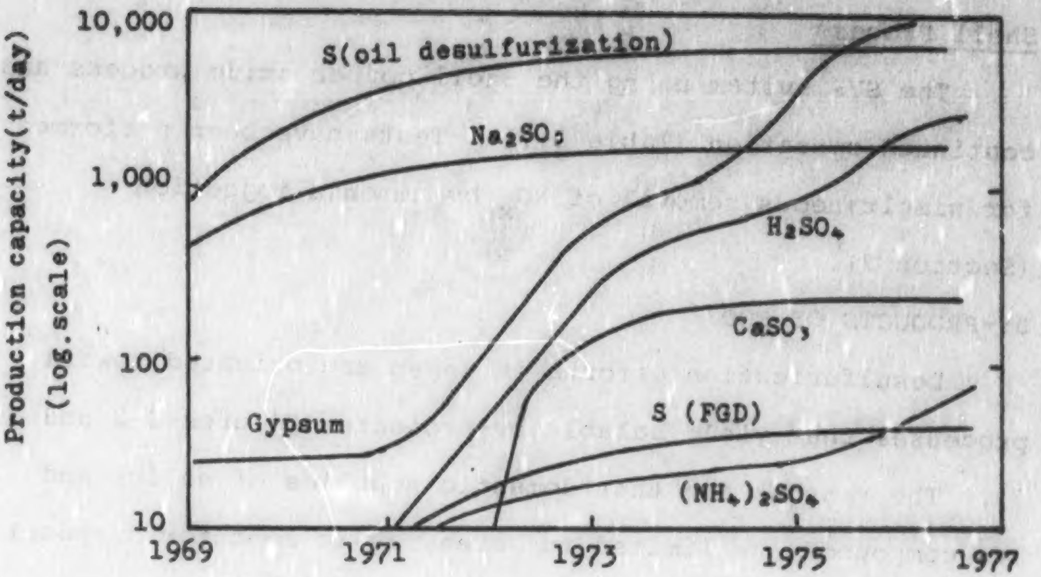

Figure 3-2. Production capacity of desulfurization.

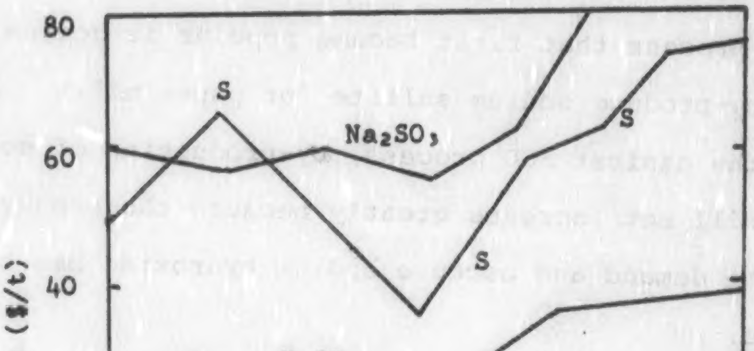

Figure 3-3. Price of by-products.

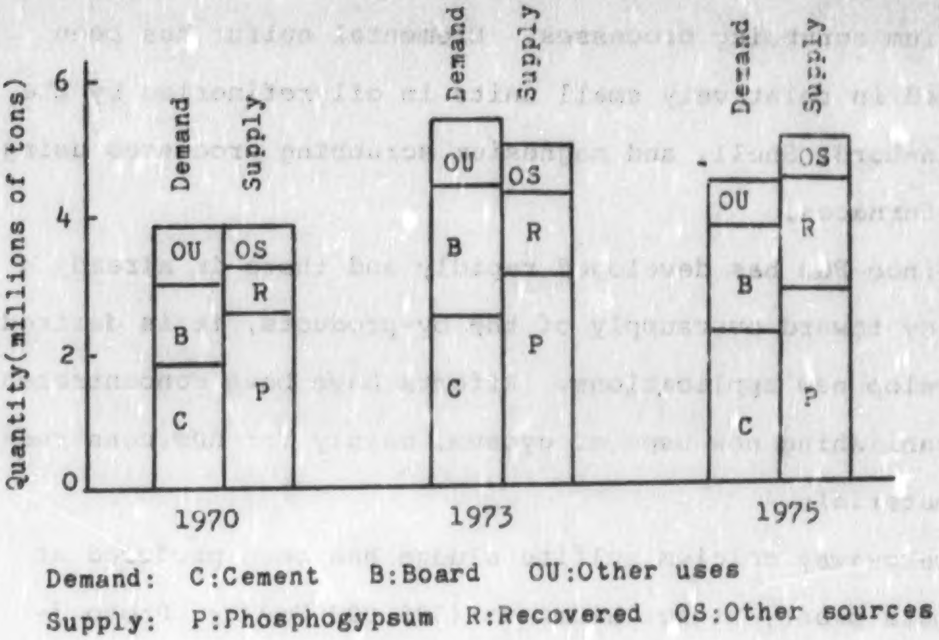

Figure 3-4. Demand for and supply of gypsum in Japan.

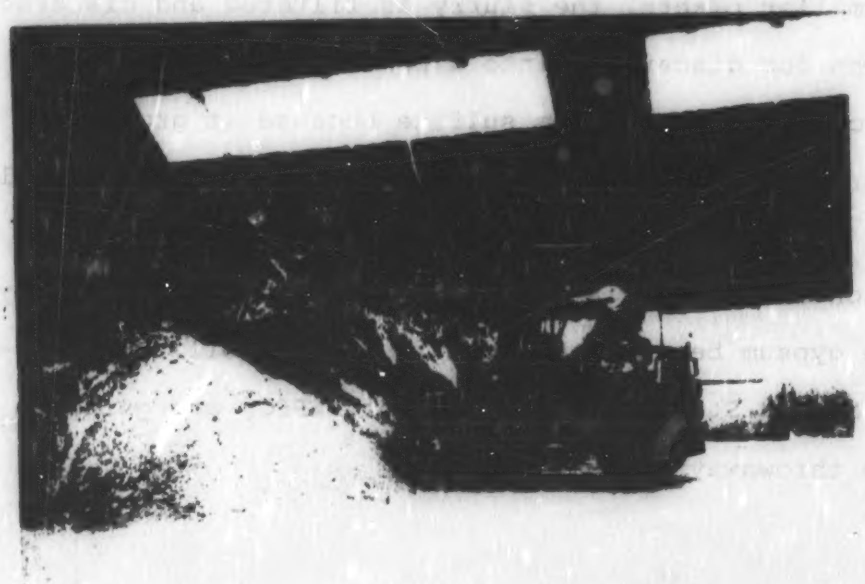

Photo 3-1. Handling of by-product gypsum (Chiba plant, Showa Denko).

Sulfuric acid has been produced by the Wellman-Lord and magnesium scrubbing processes. Elemental sulfur has been produced in relatively small units in oil refineries by the Wellman-Lord, Shell, and magnesium scrubbing processes using Claus furnaces.

Since FGD has developed rapidly and there is already a tendency toward oversupply of the by-products, it is desired to develop new applications. Efforts have been concentrated on establishing new uses of gypsum, mainly for new construction materials.

Throwaway calcium sulfite sludge has been produced at the Omuta plant, Mitsui Aluminum (385,000 $Nm^3$/hr, Photo 3-2), where the sulfite slurry is discharged into a large pond and the supernatant is recycled to the scrubber. In two other smaller plants, the slurry is filtered and discarded.

Even for discarding into a pond, gypsum might be a better choice than calcium sulfite because it grows into much larger crystals and readily settles into a much smaller volume. The Omura plant, Mitsui Aluminum, that has been in operation since 1972 is going to change the process to by-produce gypsum because the pond is nearly full. The Wakamatsu plant, Nippon Steel, and Isogo plant, EPDC, are going to produce throwaway gypsum.

**Photo 3-2. Calcium sulfite sludge disposal (Omuta plant, Mitsui Aluminum).**

## WASTEWATER AND GAS REHEATING

### Wastewater

Most Japanese FGD processes purge wastewater, as shown in Table 3-8 and Figure 3-5, mainly to prevent the accumulation of impurities, especially chloride, in the circulating liquor. Chloride, which is derived from fuel and process water, promotes corrosion, particularly when the liquor contains more than 1 ppm of oxygen, as shown in Figure 3-6.

Plants using the Kureha-Kawasaki process (Section 4) do not normally purge any water because the scrubber liquor is very low in oxygen. Chloride concentrations in the liquor at those plants has reached 4,000 ppm; the amount of chloride leaving the system with gypsum which contains 6 to 8 percent moisture has become equal to that going into the system. Another process free from wastewater is the Kobe Steel process (Section 5), which uses a calcium chloride solution dissolving lime as the absorbent and uses highly corrosion-resistant materials for construction of system components.

The dry processes are not free from wastewater, except for the Sumitomo Heavy Industry process, which uses carbon absorption and thermal regeneration. The Tokyo Electric - Hitachi and the Shell processes give relatively large amounts of wastewater because they use wet treatment in the regeneration steps.

## Table 3-8. WASTEWATER FROM FGD SYSTEMS

| Process | User | Plant site | MW | Inlet $SO_2$, ppm | Wastewater t/hr (A) | Gypsum, t/hr Solid (B) | Gypsum, t/hr Moisture (C) | Water ratio $\frac{(A+C)}{(A+B+C)}$ | Wastewater kg/MWhr |
|---|---|---|---|---|---|---|---|---|---|
| Mitsubishi (MHI) | Kansai Electric | Kainan | 150 | 270 | 1.5 | 0.9 | 0.1 | 0.64 | 10 |
| | Kyushu Electric | Karita | 188 | 600 | 3.7 | 2.2 | 0.2 | 0.64 | 20 |
| | Chubu Electric | Owase[a] | 750 | 1,480 | 14.0 | 29.0 | 2.9 | 0.37 | 19 |
| Mitsui-Chemico | EPDC | Takasago[b] | 250 | 1,500 | 5.0 | 10.0 | 1.1 | 0.38 | 20 |
| Babcock-Hitachi | Chugoku Electric | Mizushima | 105 | 400 | 1.5 | 0.9 | 0.1 | 0.64 | 14 |
| | Chugoku Electric | Tamashima | 500 | 1,500 | 5.0 | 19.5 | 1.9 | 0.26 | 10 |
| Chubu-MKK | Ishihara Chemical | Yokkaichi | 85 | 1,300 | 3.5 | 2.2 | 0.2 | 0.62 | 41 |
| Showa Denko | Showa Denko | Chiba | 150 | 1,400 | 3.5 | 5.2 | 0.5 | 0.45 | 23 |
| Chiyoda | Hokuriku Electric | Toyama | 250 | 610 | 15.0 | 7.5 | 0.7 | 0.73 | 60 |
| | Hokuriku Electric | Fukui | 350 | 1,540 | 24.0 | 14.0 | 1.4 | 0.64 | 68 |
| Wellman-MKK | Chubu Electric | Nishinagoya | 220 | 1,800 | 3.0 | | | | 14 |

[a] Designed value; the plant has just started operation.

[b] Coal-fired boiler. All others are for oil-fired boilers.

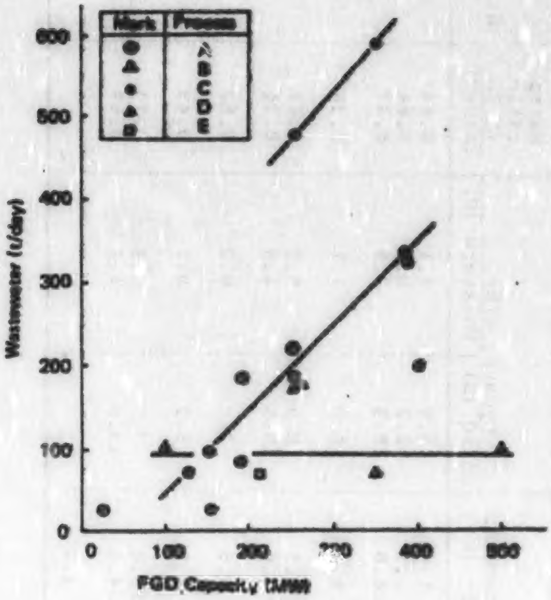

Figure 3-5. FGD capacity and amount of wastewater.[6]

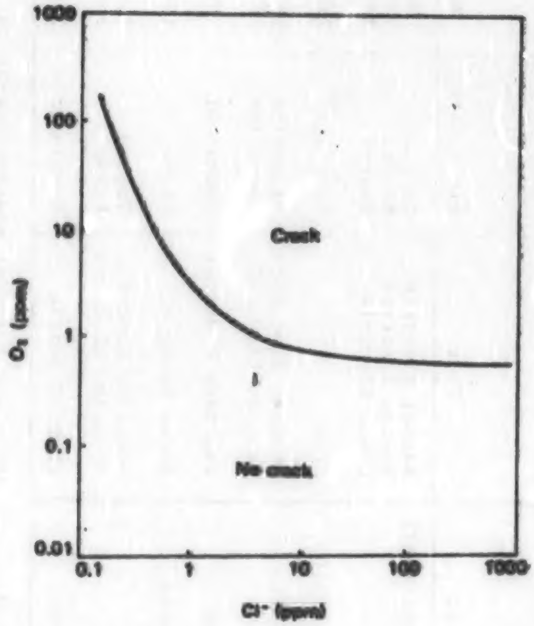

Figure 3-6. Concentration of $O_2$ and $Cl^-$ in solution and stress corrosion.

Many states in the United States prohibit the discharge of wastewater but allow the discarding of calcium sulfite sludge after filtration; the sludge usually contains 50 to 60 percent water (water ratio 0.5 to 0.6). Although most Japanese processes purge some wastewater, the amount is about equal to or even less than that purged by sludge disposal. The Chiyoda process normally purges a larger amount of water to prevent corrosion because Chiyoda uses sulfuric acid saturated with oxygen as the absorbent. The volume of wastewater can be reduced by using a material with greater corrosion resistance.

Wastewater is treated to meet regulations. The treatment in most processes is simple, consisting principally of neutralization and filtration. Some processes, such as the Wellman-Lord process, require extensive treatment including ozone oxidation to decompose reducing compounds formed in the process. After being treated, the wastewater normally has a pH of 6 to 8.5, contains 5 to 20 mg/liter of SS (suspended solids), contains less than 10 mg/liter of COD (chemical oxygen demand), and does not adversely affect the environment.

## Reheating

The temperature of boiler flue gas that has passed through an air preheater and electrostatic precipitator normally ranges from 130 to 150°C. Scrubbing in the wet processes usually reduces the gas temperature to 50 to 60°C. In most systems the gas is heated to 110 to 150°C by afterburning of low-sulfur oil. Although afterburning is the easiest way to reheat stack gas, the oil requirement reaches 3 to 5 percent of that used for the boiler. Afterburning not only is somewhat costly but adds $SO_2$ and dust to the cleaned gas.

A few companies have made tests on reheating the gas using a gas-steam heat exchanger. Corrosion of the heat exchanger tubes is the major problem, particularly when the scrubber liquor is rich in chloride. Commercial use of such heat exchangers will start soon.

## ECONOMIC ASPECTS OF FGD SYSTEMS

Among the various FGD processes, the sodium scrubbing process that by-produces sodium sulfite is the simplest and also the least expensive. The second cheapest, the throwaway wet-lime process, requires a large disposal pond. A system based on the wet lime-gypsum process costs about 25 percent more than one using the throwaway process, but does not require a pond.

Examples of plant cost in battery limits are shown in Table 3-9. The cost rose sharply until the middle of 1975 because of inflation and the active demand for FGD units, but has since lowered considerably. Generally speaking, a

Table 3-9. PLANT COST IN BATTERY LIMITS (\$1 = ¥300)

(The cost nearly tripled in late 1973 and has decreased considerably since late 1975)

| Process | Absorbent | By-product | Capacity, MW | Plant cost M \$ | Plant cost \$/kW | Year completed |
|---|---|---|---|---|---|---|
| Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 70 | 2.6 | 37 | 1971 |
| Sumitomo S.B. | Carbon | $H_2SO_4$ | 55 | 2.8 | 51 | 1971 |
| Chemico-Mitsui | $Ca(OH)_2$ | Sludge | 128 | 3.3 | 26 | 1972 |
| Hitachi-Tokyo E.P. | Carbon | Gypsum | 150 | 5.6 | 39 | 1972 |
| Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 220 | 7.0 | 32 | 1973 |
| Shell | CuO | $SO_2$ | 40 | 3.3 | 83 | 1973 |
| Chubu-MKK | $CaCO_3$ | Gypsum | 89 | 2.6 | 29 | 1973 |
| Chemico-Mitsui | MgO | $SO_2$ | 180 | 13 | 72 | 1974 |
| Mitsui-Chemico | $CaCO_3$ | Gypsum | 250 | 16 | 64 | 1974 |
| Mitsubishi (MHI) | CaO | Gypsum | 188 | 11.5 | 61 | 1974 |
| Kureha-Kawasaki | $Na_2SO_3$ | Gypsum | 450 | 32 | 71 | 1975 |
| Chiyoda | $H_2SO_4$ | Gypsum | 350 | 26 | 74 | 1975 |
| Babcock-Hitachi | $CaCO_3$ | Gypsum | 500 | 35 | 70 | 1975 |
| Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 160 | 20 | 125 | 1975 |

wet lime-gypsum process unit (200-300 MW) now costs $45 to $60/kW in batterly limits; system based on the indirect lime/limestone process costs 5 to 30 percent more, and one using sulfuric acid by-production processes costs 30 to 70 percent more than the wet lime-gypsum process.

Examples of FGD costs for removal of 90 to 95 percent of the $SO_2$ by the wet lime-gypsum process are shown in Table 3-10. The cost is about $14 to $17/kl oil or 3.0 to 3.6 mil/kWh for different sizes of unit, based on 7 years depreciation and 7,000 hours yearly operation. As the fixed cost is greater than the running cost, the FGD cost is largely influenced by years of depreciation and by operating hours.

Capital cost of the wet limestone-gypsum process may be slightly higher than those of the lime-gypsum process, but operating costs are slightly lower. Indirect lime/limestone processes usually cost 5 to 20 percent more than does the lime-gypsum process. Sulfuric acid by-producing processes cost 20 to 30 percent more.

The current per-kiloliter price of heavy oil is about $75 for high-sulfur oil (S=3%) and $100 for low-sulfur oil (S=0.3%). Therefore, FGD is more economical than the use of low-sulfur oil (Table 1-6).

## Table 3-10. EXAMPLES OF FGD COST WITH WET LIME-GYPSUM PROCESS

(7 years depreciation, 7,000 hours full-load operation per year. Oil consumption: 150,000 kl/100 MW/year, S: 2.8%, 90% removal. Reheating to 110°C).

| | 100 MW | 500 MW |
|---|---|---|
| Investment cost, $1,000 | 6,600 | 27,000 |
| Fixed cost, $1,000/year | | |
| Depreciation | 940 | 3,860 |
| Interest, Insurance | 470 | 1,930 |
| Total | 1,410 | 5,790 |
| Running cost, $1,000/year | | |
| Lime (at $30/t) | 230 | 1,140 |
| Oil for reheating (at $100/kl) | 450 | 2,230 |
| Power (at 3¢/kWh) | 400 | 1,840 |
| Labor | 50 | 50 |
| Maintenance | 100 | 300 |
| Other requirements | 20 | 60 |
| Gypsum (at $5/t) | -120 | -610 |
| Total | 1,130 | 5,010 |
| Total annual cost, $1,000 | 2,540 | 10,800 |
| Desulfurization cost, $/kl | 16.9 | 14.4 |
| Desulfurization cost, mills/kWhr | 3.6 | 3.0 |

Flue gas desulfurization (FGD) is less expensive than hydrodesulfurization (HDS) at higher sulfur removal ratios (Table 2-4), but HDS is advantageous in that it produces elemental sulfur, which is a desirable by-product. In Japan and elsewhere, other processes yielding sulfur as a by-product seem much more expensive than HDS, except for oil refineries that have Claus furnaces for sulfur production.

## 4. MAJOR NEW FGD SYSTEMS FOR UTILITY BOILERS

### STATUS OF FGD BY POWER COMPANIES

Table 4-1 lists power companies and their capacities for steam power generation and FGD. The nine major companies (Nos. 1 to 9 in the Table) have produced about 70 percent of the total steam power using mainly oil, with some LNG and a little coal. Electric Power Development Co. (EPDC, No. 10 in the Table), which was established by the nine major companies and the Central Government, has been the major consumer of domestic coal for power generation. Other power suppliers have relatively small capacities, burning mainly oil. Total capacity of the power generation plants, including those under construction and planned for construction, is 86,457 MW. The capacity of FGD systems in operation is 6,040 MW and that of systems under construction and being designed is 6,755 MW.

Among the major power companies, Tokyo Electric, Kansai Electric, and Chubu Electric, which supply power to the largest cities and industrial complexes in Japan, have relatively small capacities of FGD, with a B/A ratio (see Table 4-1) of only 1 to 7 percent. Those companies prefer

## Table 4-1. CAPACITIES OF STEAM POWER GENERATION AND FGD OF POWER COMPANIES

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| No. | Power company | Power generation, MW |  |  | FGD, MW |  |  | B/A[b] (%) |
|---|---|---|---|---|---|---|---|---|
|  |  | Existing | Under construction[a] | Total (A) | Existing | Under construction[a] | Total (B) |  |
| 1 | Hokkaido | 1,270 | 1,225 | 2,495 | 0 | 525 | 525 | 21.0 |
| 2 | Tohoku | 3,925 | 1,200 | 5,125 | 275 | 625 | 900 | 17.6 |
| 3 | Tokyo | 19,167 | 4,400 | 23,567 | 283 | 0 | 0 | 1.2 |
| 4 | Chubu | 9,933 | 3,800 | 13,733 | 970 | 0 | 970 | 7.1 |
| 5 | Hokuriku | 1,412 | 1,000 | 2,412 | 600 | 500 | 1,100 | 45.6 |
| 6 | Kansai | 10,672 | 1,200 | 11,872 | 369 | 469 | 838 | 7.1 |
| 7 | Chugoku | 3,777 | 1,800 | 5,777 | 950 | 1,100 | 2,050 | 36.8 |
| 8 | Shikoku | 2,687 | 450 | 3,137 | 900 | 0 | 900 | 12.5 |
| 9 | Kyushu | 4,500 | 2,700 | 7,200 | 188 | 1,438 | 1,626 | 22.6 |
| 10 | EPDC | 1,430 | 0 | 1,430 | 780 | 500 | 1,280 | 89.5 |
| 11 | Niigata | 350 | 350 | 700 | 175 | 175 | 350 | 50.0 |
| 12 | Showa | 550 | 0 | 550 | 150 | 250 | 400 | 72.7 |
| 13 | Toyama | 750 | 0 | 750 | 250 | 0 | 250 | 33.3 |
| 14 | Mizushima | 462 | 0 | 462 | 156 | 0 | 156 | 33.8 |
| 15 | Sumitomo | 368 | 250 | 618 | 0 | 218 | 218 | 35.3 |
| 16 | Sakata | 0 | 700 | 700 | 0 | 700 | 700 | 100.0 |
| 17 | Fukui | 0 | 250 | 250 | 0 | 250 | 250 | 100.0 |
| 18 | Others | 5,512 | 375 | 5,887 | 0 | 0 | 0 | 0.0 |
|  | Total | 66,775 | 19,700 | 85,475 | 6,040 | 6,755 | 12,795 | 14.8 |

[a] Including those decided to be constructed.

[b] Capacity being scrubbed over total capacity.

use of low-sulfur fuels such as naphtha and LNG in polluted areas, because they believe that the regulation on $SO_2$ emission for those areas may become too stringent to be achieved by FGD. According to the recent regulation restricting total mass emissions of $SO_2$, large power plants in the designated regions are required to keep $SO_2$ in flue gas below about 50 ppm, as described in Section 1. Although it is not difficult to reduce $SO_2$ from 1,500 ppm to 50 ppm by FGD, sulfur-free fuel is needed to reheat the treated gas. For plants to be constructed in regions to which much more stringent restriction is applied, FGD may entail some difficulty. On the other hand, Hokuriku Electric and Chugoku Electric, which have power plants remote from big cities, have larger B/A ratios (refer to Table 4-1).

FGD installations of power companies are listed in Table 4-2. Before 1973 power companies were not yet confident about the usefulness of FGD and therefore constructed test units to treat one-third to one-fourth of the gas from a boiler burning low-sulfur fuel; other industries that had difficulty in obtaining low-sulfur fuel constructed many FGD systems and demonstrated their reliability. The first commercial-scale FGD system for a utility boiler burning high-sulfur fuel was the Nishinagoya plant, Chubu Electric Power (200 MW, 620,000 $Nm^3$/hr) based on the Wellman-Lord

## Table 4-2. FGD SYSTEMS OF POWER COMPANIES

(Oil-fired boilers unless otherwise indicated)

| Power company | Power station | Boiler | | FGD MW | Process developer | Absorbent, precipitant | By-product | Year of completion |
|---|---|---|---|---|---|---|---|---|
| | | No. | MW | | | | | |
| Tohoku | Sinsendai | 2 | 600 | 150 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1974 |
| | Hachinohe | 4 | 250 | 125 | Mitsubishi H.I. | CaO | Gypsum | 1974 |
| | Niigata | 4 | 250 | 125 | Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 1975 |
| | Niigata H. | 1 | 600 | 150 | Mitsubishi H.I. | $CaCO_3$ | Gypsum | 1976 |
| | Akita | 3 | 350 | 350 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1977 |
| Tokyo | Kashima | 3 | 600 | 350 | Hitachi-Tokyo | Carbon, $CaCO_3$ | Gypsum | 1972 |
| | Yokosuka | 1 | 265 | 132 | Mitsubishi H.I. | $CaCO_3$ | Gypsum | 1974 |
| Chubu | Nishinagoya | 1 | 220 | 220 | Wellman-MKK | $Na_2SO_3$ | $H_2SO_4$ | 1973 |
| | Owase | 1 | 375 | 375 | Mitsubishi H.I. | CaO | Gypsum | 1976 |
| | Owase | 2 | 375 | 375 | Mitsubishi H.I. | CaO | Gypsum | 1976 |
| Hokuriku | Toyama | 1 | 500 | 250 | Chiyoda | $H_2SO_4$, $CaCO_3$ | Gypsum | 1974 |
| | Fukui | 1 | 350 | 350 | Chiyoda | $H_2SO_4$, $CaCO_3$ | Gypsum | 1975 |
| | Nanao | 1 | 500 | 500 | Not decided | | Gypsum | 1978 |
| Kansai | Sakai | 8 | 250 | 63 | Sumitomo H.I. | Carbon | $H_2SO_4$ | 1972 |
| | Amagasaki | 2 | 156 | 35 | Mitsubishi H.I. | CaO | Gypsum | 1973 |
| | Amagasaki | | | 121 | Mitsubishi H.I. | CaO | Gypsum | 1975 |
| | Amagasaki | 1 | 156 | 156 | Mitsubishi H.I. | CaO | Gypsum | 1976 |
| | Osaka | 3 | 156 | 156 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1975 |
| | Osaka | 2 | 156 | 156 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1975 |
| | Osaka | 4 | 156 | 156 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1976 |
| | Kainan | 4 | 600 | 150 | Mitsubishi H.I. | CaO | Gypsum | 1974 |
| Chugoku | Mizushima | 2 | 156 | 100 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1974 |
| | Tamashima | 3 | 500 | 500 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1975 |
| | Tamashima | 2 | 350 | 350 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1976 |
| | Shimonoseki | 2 | 400 | 400 | Mitsubishi H.I. | $CaCO_3$ | Gypsum | 1976 |
| Shikoku | Anan | 3 | 450 | 450 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1975 |
| | Sakaide | 3 | 450 | 450 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1975 |

use of low-sulfur fuels such as naphtha and LNG in polluted areas, because they believe that the regulation on $SO_2$ emission for those areas may become too stringent to be achieved by FGD. According to the recent regulation restricting total mass emissions of $SO_2$, large power plants in the designated regions are required to keep $SO_2$ in flue gas below about 50 ppm, as described in Section 1. Although it is not difficult to reduce $SO_2$ from 1,500 ppm to 50 ppm by FGD, sulfur-free fuel is needed to reheat the treated gas. For plants to be constructed in regions to which much more stringent restriction is applied, FGD may entail some difficulty. On the other hand, Hokuriku Electric and Chugoku Electric, which have power plants remote from big cities, have larger B/A ratios (refer to Table 4-1).

FGD installations of power companies are listed in Table 4-2. Before 1973 power companies were not yet confident about the usefulness of FGD and therefore constructed test units to treat one-third to one-fourth of the gas from a boiler burning low-sulfur fuel; other industries that had difficulty in obtaining low-sulfur fuel constructed many FGD systems and demonstrated their reliability. The first commercial-scale FGD system for a utility boiler burning high-sulfur fuel was the Nishinagoya plant, Chubu Electric Power (200 MW, 620,000 $Nm^3$/hr) based on the Wellman-Lord

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## Table 4-2 (continued). FGD SYSTEMS OF POWER COMPANIES

(Oil-fired boilers unless otherwise indicated)

| Power company | Power station | Boiler | | FGD MW | Process developer | Absorbent, precipitant | By-product | Year of completion |
|---|---|---|---|---|---|---|---|---|
| | | No. | MW | | | | | |
| Kyushu | Karita | 2 | 375 | 188 | Mitsubishi H.I. | CaO | Gypsum | 1974 |
| | Karatsu | 2 | 375 | 188 | Mitsubishi | $CaCO_3$ | Gypsum | 1975 |
| | Karatsu | 3 | 500 | 250 | Mitsubishi | $CaCO_3$ | Gypsum | 1976 |
| | Ainoura | 1 | 375 | 250 | Mitsubishi | $CaCO_3$ | Gypsum | 1976 |
| | Ainoura | 2 | 500 | 250 | Mitsubishi | $CaCO_3$ | Gypsum | 1976 |
| | Buzen | 1 | 500 | 250 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1977 |
| | Buzen | 2 | 500 | 250 | Kureha-Kawasaki | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1978 |
| EPDC | Takasago | 1 | 250[a] | 250 | Mitsui-Chemico | $CaCO_3$ | Gypsum | 1975 |
| | Takasago | 2 | 250[a] | 250 | Mitsui-Chemico | $CaCO_3$ | Gypsum | 1976 |
| | Isogo | 1 | 265[a] | 265 | Chemico-IHI | $CaCO_3$ | Gypsum | 1976 |
| | Isogo | 2 | 265[a] | 265 | Chemico-IHI | $CaCO_3$ | Gypsum | 1976 |
| | Takehara | 1 | 250[a] | 250 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1977 |
| Niigata | Niigata | 1 | 350 | 175 | MHI | $CaCO_3$ | Gypsum | 1975 |
| Showa | Ichihara | 1 | 150 | 150 | Showa Denko | $Na_2SO_3$, $CaCO_3$ | Gypsum | 1973 |
| | Ichihara | 5 | 250 | 250 | Babcock-Hitachi | $CaCO_3$ | Gypsum | 1976 |
| Toyama | Toyama | 1 | 250 | 250 | Chiyoda | $H_2SO_4$, $CaCO_3$ | Gypsum | 1975 |
| Mizushima | Mizushima | 5 | 156 | 156 | Mitsubishi H.I. | CaO | Gypsum | 1975 |
| Sumitomo | Niihama | 3 | 156 | 156 | IHI | $CaCO_3$ | Gypsum | 1975 |
| Sakata | Sakata | 1 | 350 | 350 | Mitsubishi H.I. | $CaCO_3$ | Gypsum | 1976 |
| | | 2 | 350 | 350 | Mitsubishi H.I. | $CaCO_3$ | Gypsum | 1977 |
| Fukui | Fukui | 1 | 250 | 250 | Not decided | $CaCO_3$ | Gypsum | 1977 |

[a] Coal-fired boilers.

process. The system has been operated smoothly at more than 97 percent operability. As regulations on wastewater have become increasingly stringent, however, wastewater treatment has posed a serious problem in the Wellman-Lord process.

Since 1973, power companies have constructed many full-scale FGD systems for utility boilers (250-500 MW) burning high-sulfur fuel (2.5 to 3 percent sulfur) using processes that produce gypsum. Processes and performance of several new FGD systems are described below.

In addition to the systems described in this section two units at Isogo Station, Electric Power Development Co., started operation very recently. These systems have a unit capacity of treating 900,000 $Nm^3$/hr of flue gas from a coal-fired boiler using the Chemico-IHI process; no additional details are available.

## PLANTS USING THE MHI LIME-GYPSUM PROCESS (MITSUBISHI-JECCO PROCESS)[2]

### Karita Plant, Kyushu Electric[8]

The Karita plant, with a capacity of treating 550,000 $Nm^3$/hr of flue gas from an oil-fired boiler (188 MW equivalent), went into operation in November 1974. The plant is based on the single-absorber system (Figure 4-1, Photo 4-1) and uses lime. Flue gas is first cooled to 55 to 60°C in a cooler and led into the plastic-grid-packed absorber. $SO_2$ concentration at the absorber inlet ranges from 400 to 600

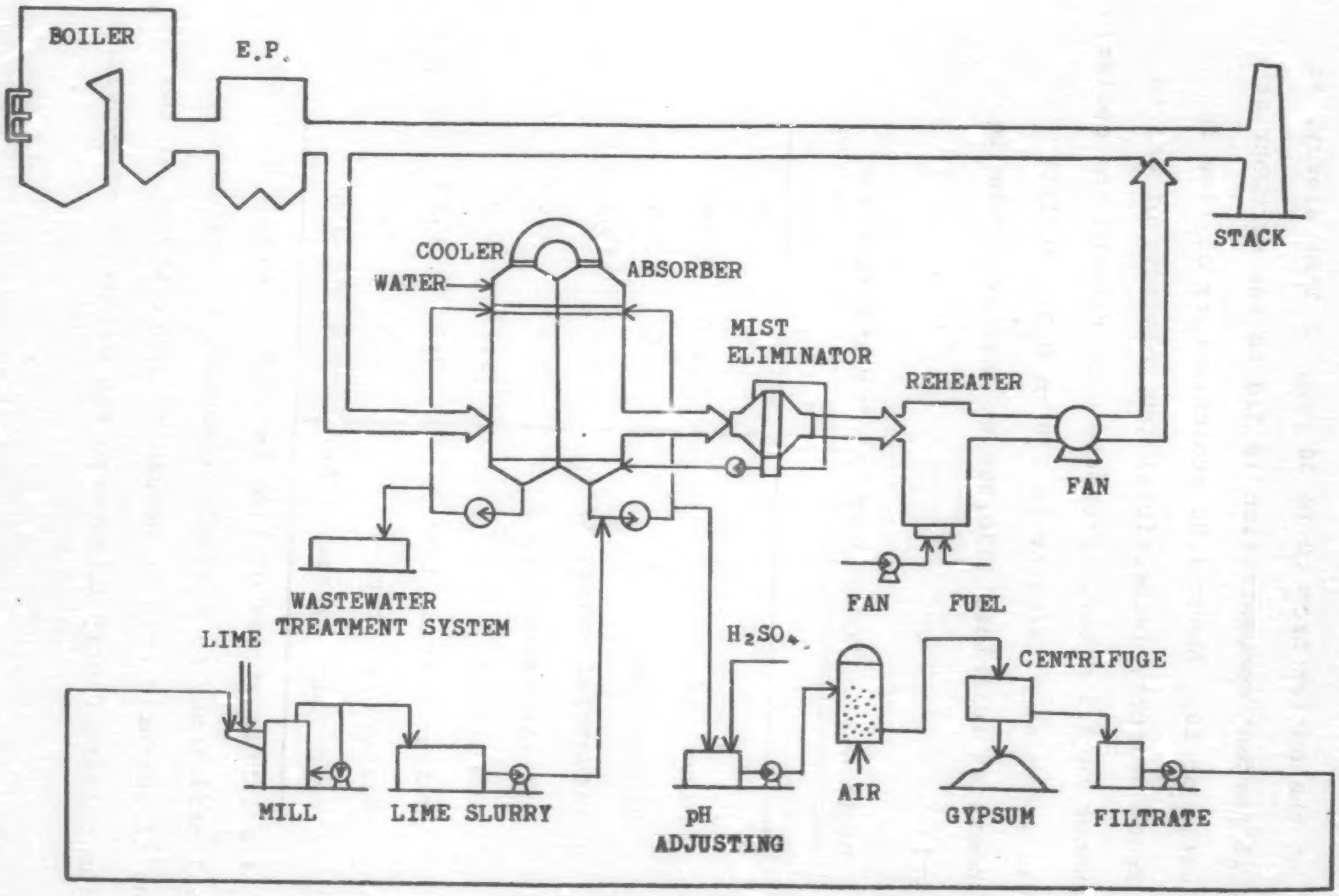

BOILER
E.P.
STACK
COOLER
WATER
ABSORBER
MIST ELIMINATOR
REHEATER
FAN
FAN
FUEL
WASTEWATER TREATMENT SYSTEM
LIME
$H_2SO_4$
CENTRIFUGE
MILL
LIME SLURRY
pH ADJUSTING
AIR
GYPSUM
FILTRATE

Figure 4-1. One-absorber system of MHI process.

ppm and at the outlet from 10 to 30 ppm. A lime slurry, at pH 6.4, 10 percent concentration is fed to the scrubber at an L/G ratio of 10. About 1.05 stoichiometry of lime is used. Space velocity (superficial gas velocity) of gas in the scrubber is 3.5 m/sec. Pressure drop through the cooler, absorber, and mist eliminator is 120 mm $H_2O$. Utility requirements at full load (550,000 $Nm^3$/hr) are shown in Table 4-3.

Table 4-3. REQUIREMENTS AT THE KARITA PLANT

| | Sulfur in fuel, % | |
|---|---|---|
| | 1.2 | 0.8 |
| Power, kW | 3,200 | 3,200 |
| Steam, t/hr | 1.5 | 1.5 |
| Industrial water, t/hr | 3.0 | 3.0 |
| Oil for reheating, t/hr | 2.0 | 2.0 |
| Lime, t/hr | 1.1 | 0.8 |
| Sulfuric acid, t/hr | 0.2 | 0.13 |
| Wastewater, t/hr | 3.5 | 3.5 |
| By-product gypsum, t/hr | 2.9 | 2.0 |

As a little excess of lime is used to ensure high $SO_2$ removal efficiency by a single absorber, a considerable amount of sulfuric acid is needed to lower the pH of the calcium sulfite slurry to promote the oxidation of gypsum.

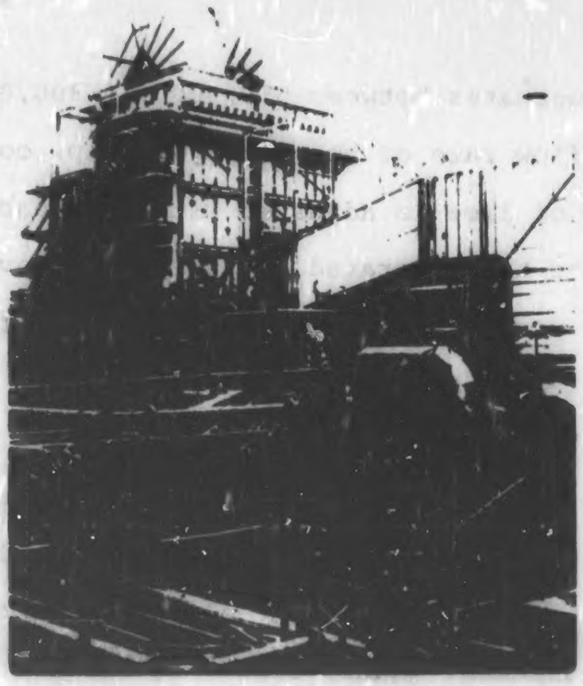


Photo 4-1. Karita plant, Kyusha Electric (188MW).

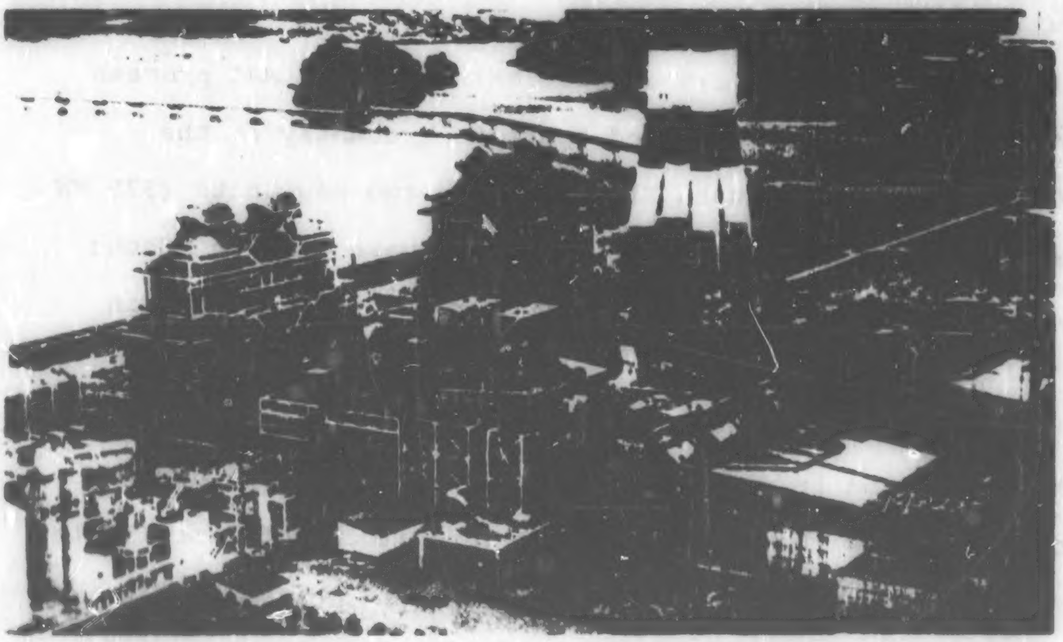


Photo 4-2. Owase Plant, Chubu Electric
(2 units each 375 MW).

The load fluctuates between 550,000 and 300,000 $Nm^3$/hr every day. The flow rate of the slurry is kept constant, while the amount of lime is adjusted with the load.

The plant has been operated at 100 percent availability since start-up, except for a scheduled shutdown of the boiler from April 1 to May 14, 1975 (Figure 4-2). On February 24, 1975, a flow-rate-adjusting bulb was stopped up but was repaired without interrupting scrubber operation. In the inspection of April 1975, considerable scaling was found on the mist eliminators. The eliminators had been washed with circulating liquor; since May 1975, in an effort to reduce scaling, they have been washed alternately with the liquor and fresh water. Water balance is shown in Figure 4-3.

## Other Plants

Two new units (175 and 250 MW) using the MHI process with limestone have started operation recently at the Karatsu station, Kyushu Electric, and two new units (375 MW each) using lime have started at the Owase station, Chubu Electric (Photo 4-2). Operating parameters are shown in Table 3-5.

The units at Owase have a two-tower system.[2] $SO_2$ concentration is reduced from 1,600 ppm to 30 ppm using slightly less than the stoichiometric amount of lime (Table

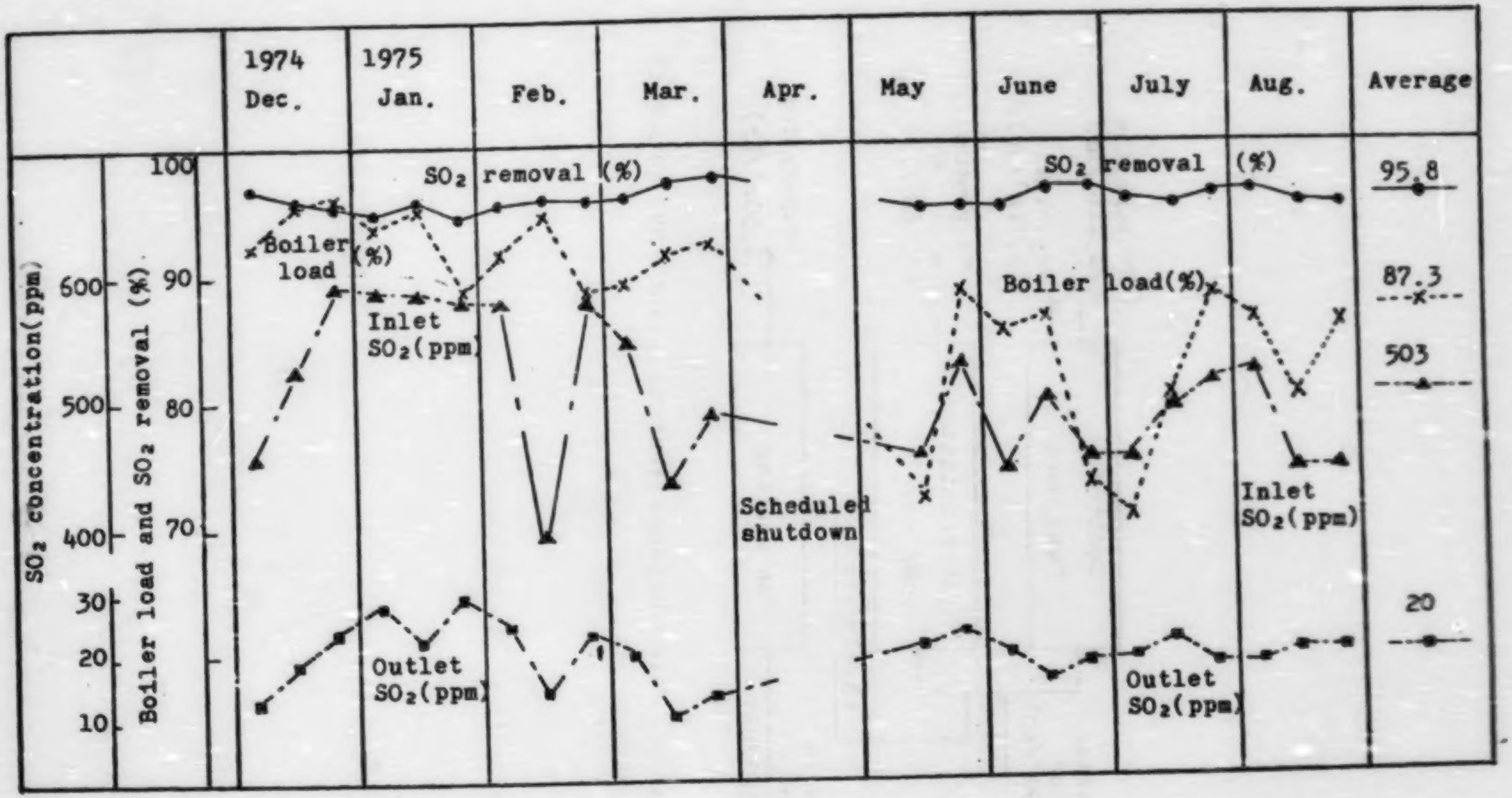


Figure 4-2. Operation data fo Karita plant, Kyushu Electric.

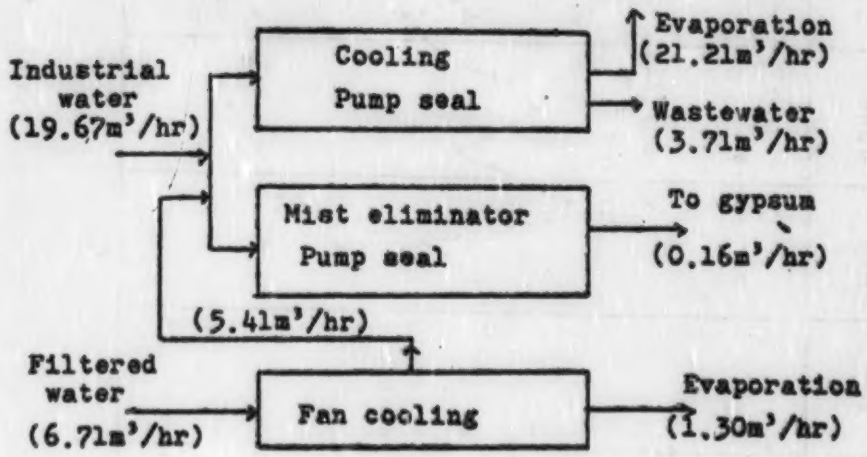

Industrial water
(19.67m³/hr)
Cooling
Pump seal
Evaporation
(21.21m³/hr)
Wastewater
(3.71m³/hr)
Mist eliminator
Pump seal
To gypsum
(0.16m³/hr)
(5.41m³/hr)
Filtered water
(6.71m³/hr)
Fan cooling
Evaporation
(1.30m³/hr)

Figure 4-3. Water balance (Karita plant, MHI process).

3-5) at a pressure drop of 200 mm $H_2O$. No sulfuric acid is required because about 99 percent of the lime reacts and the pH of the calcium sulfite solution is lowered considerably by the use of two absorbers and also by the high concentration of $SO_2$ at the inlet.

## MITSUI-CHEMICO LIMESTONE-GYPSUM PROCESS AT THE TAKASAGO PLANT, ELECTRIC POWER DEVELOPMENT CO.[2]

### Process and Plant Design

This plant is based on the Mitsui-Chemico process developed by Mitsui Miike Machinery Co. It is the first Mitsui-Chemico process unit to be used commercially for a coal-fired utility boiler, and has a capacity of treating 840,000 $Nm^3/hr$ flue gas from a 250 MW boiler. The plant consists of two single-stage Chemico scrubbers placed in series, a pH controller to reduce the pH of the calcium sulfite slurry by introducing the flue gas, and two reactors for oxidation of the sulfite to gypsum by air (Figure 4-4, Photos 4-3 and 4-4). A catalyst is used to promote both $SO_2$ removal and oxidation. The flue gas containing 1,500 ppm $SO_2$ and 80 $mg/Nm^3$ dust is passed through an electrostatic precipitator and the FGD unit to remove 90 percent of the $SO_2$ and 75 percent of the dust. Limestone, 95 percent under 325 mesh, is the absorbent. The operating parameters are shown in Table 3-5. Specifications of the principal equipment are shown in Table 4-4.

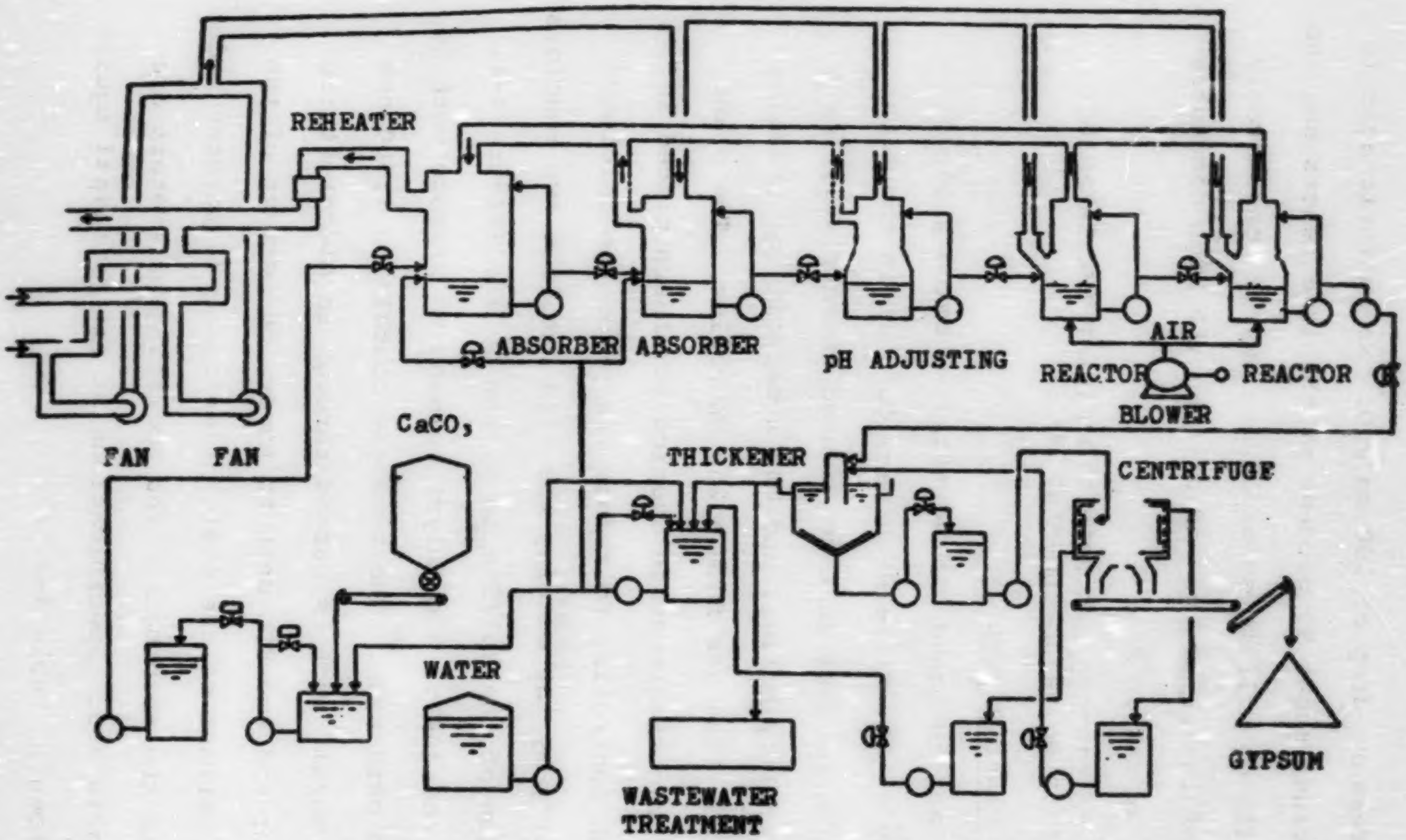

REHEATER
ABSORBER
ABSORBER
pH ADJUSTING
AIR
REACTOR
REACTOR
BLOWER
FAN
FAN
CaCO₃
THICKENER
CENTRIFUGE
WATER
WASTEWATER TREATMENT
GYPSUM

Figure 4-4. Flowsheet of Mitsui-Chemico process.

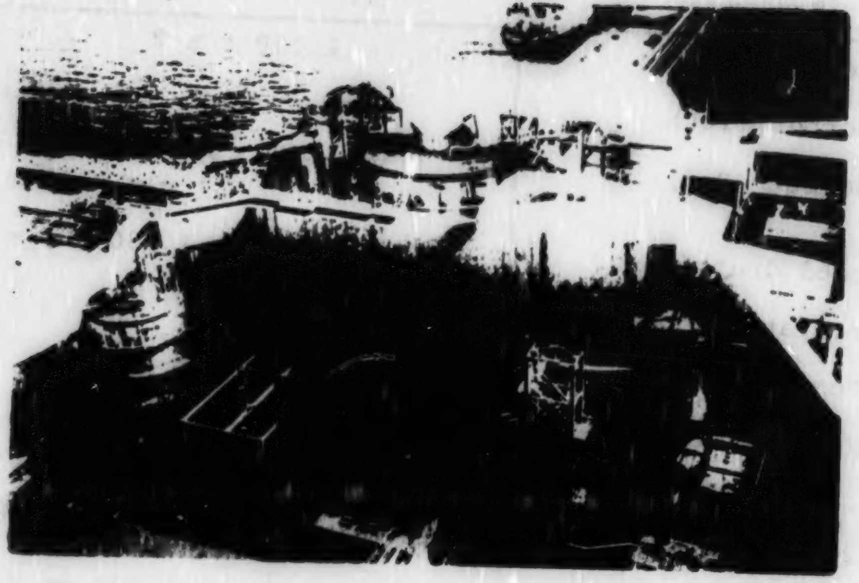


Photo 4-3. Takasago plant, EPDC (250 MW) (scrubber and reactors).

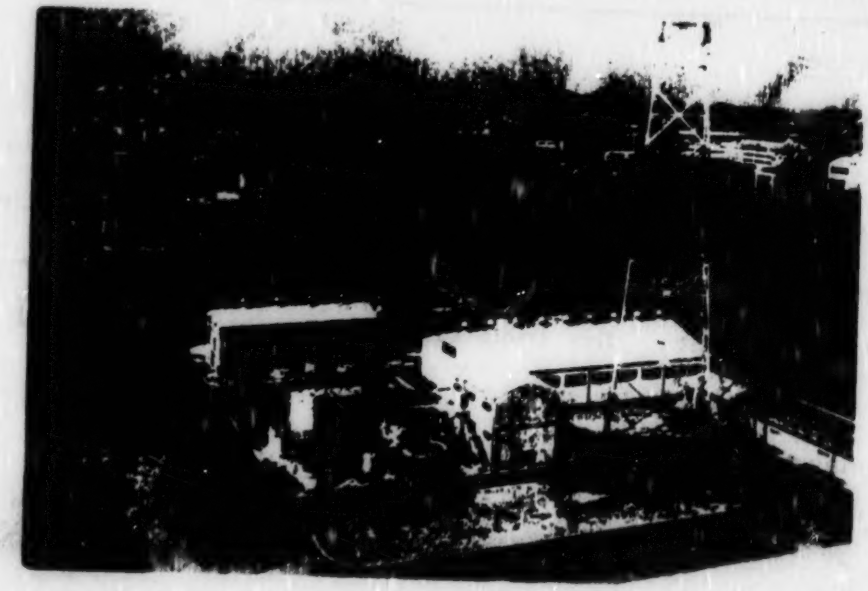


Photo 4-4. Takasago plant, EPDC (250 MW) (Gypsum centrifuge and storage).

Table 4-4. MAIN EQUIPMENT AT TAKASAGO PLANT

| Equipment | Type and dimensions |
|---|---|
| Limestone tanks | 1,000 t x 2 |
| Absorber (1st) | Venturi 11.5 m ø x 20 m |
| Absorber (2nd) | Venturi (double throat) 14 m ø x 23 m |
| Forced draft fans | (12,300 $m^3$/min, 1,900 kW) x 2 |
| Circulation pumps | |
| For 1st absorber | 135 kW x 4 |
| For 2nd absorber | 200 kW x 5 |
| pH adjusting tower | Venturi 6 m ø x 16 m |
| Reactors (oxidizers) | 6 m ø x 18 m, 2 units |
| Blowers for oxidizers | (110 $Nm^3$/hr, 1,000 mm $H_2O$, 250 kW) x 3 |
| Centrifuges | (solid 1.5 t/hr) x 7 |
| Reheating furnaces | (oil 625 liter/hr) x 4 |

Performance

The plant started up in January 1975 and has since operated well except for several brief shutdowns to clean the mist eliminators. The eliminators are washed with the circulating liquor and fresh water. System availability reaches 98 percent. The load fluctuates between 170 and 250 MW daily. The slurry flow rate in the scrubbers is kept constant.

The daily requirements for operation are as follows:

$CaCO_3$ - 118 tons
Power - 136,000 kWh
Oil - 41 liters (reheating)
Steam - 13 tons (heating of oil)
Industrial water - 1,200 tons
Catalyst - $350

The coal contains about 500 ppm chloride. To keep the chloride concentration of the scrubber liquor below 7,000 ppm, about 5 ton/hr of wastewater is purged. The relationship between the amount of purge water and the chloride concentration of coal and equilibrated scrubber liquor is shown in Figure 4-5.

To prevent promotion of corrosion by chloride, a plastic or rubber lining and a high-grade stainless steel are used.

Another plant with the same capacity is near completion at Takasago. The new plant has one reactor instead of two, as at the plant just described.

## BABCOCK-HITACHI PROCESS AT THE TAMASHIMA PLANT, CHUGOKU ELECTRIC[8]

### Process Description[2]

Hitachi Ltd. constructed a plant (500 MW full scale) using Babcock-Wilcox scrubbers and an oxidizing system to by-produce gypsum (Figure 4-6, Photos 4-5 and 4-6). Limestone, more than 95 percent under 325 mesh as shown in Table

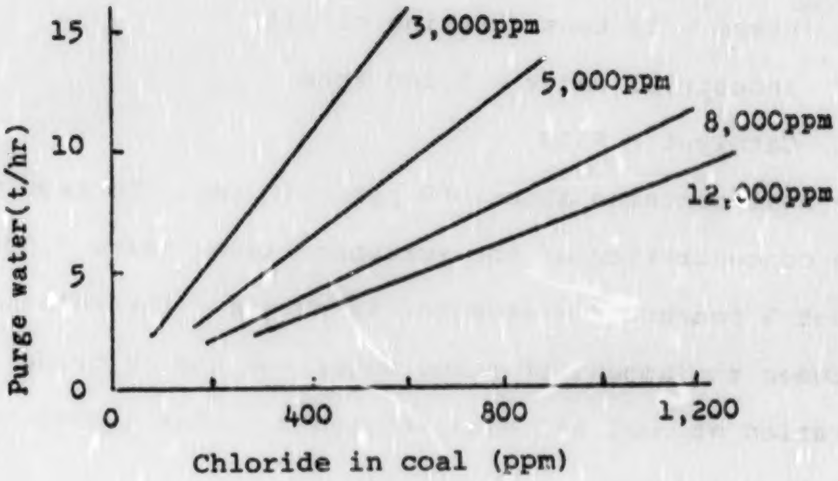


Figure 4-5. Purge water and chloride concentration.

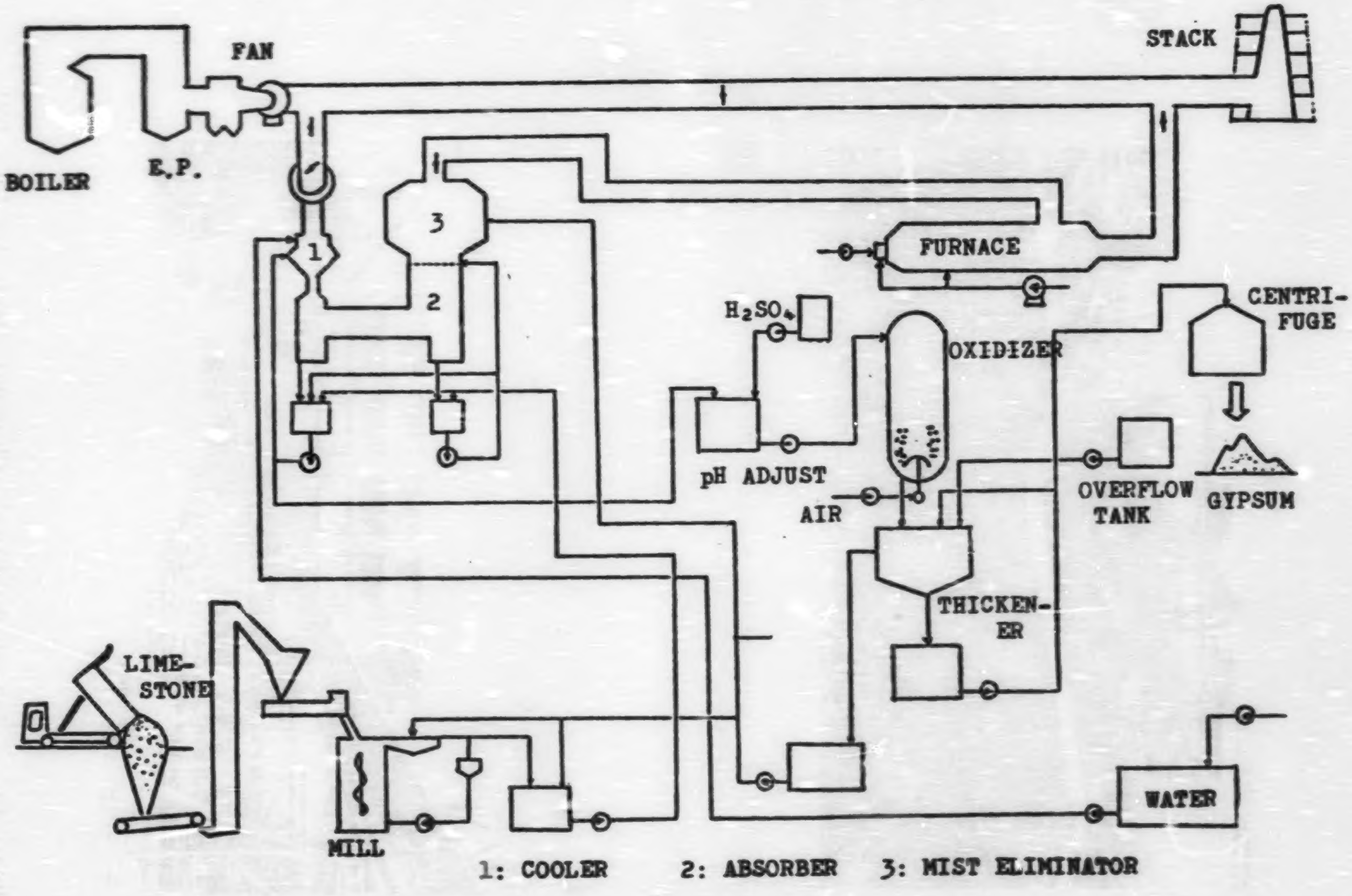

BOILER
E.P.
FAN
STACK
3
1
2
FURNACE
$H_2SO_4$
CENTRI-FUGE
OXIDIZER
pH ADJUST
AIR
OVERFLOW TANK
GYPSUM
THICKEN-ER
LIME-STONE
MILL
WATER
1: COOLER
2: ABSORBER
3: MIST ELIMINATOR

Figure 4-6. Flowsheet of Babcock-Hitachi process.

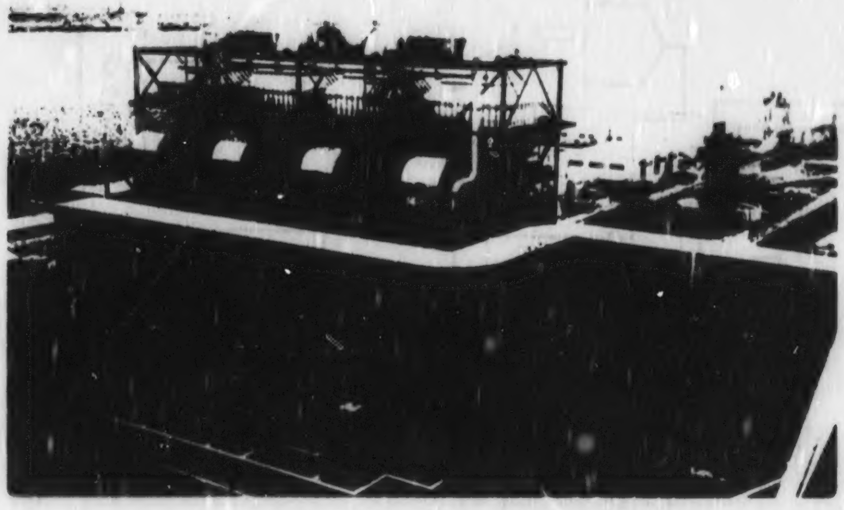


Photo 4-5. Tamashima Plant, Chugoku Electric (500 MW)

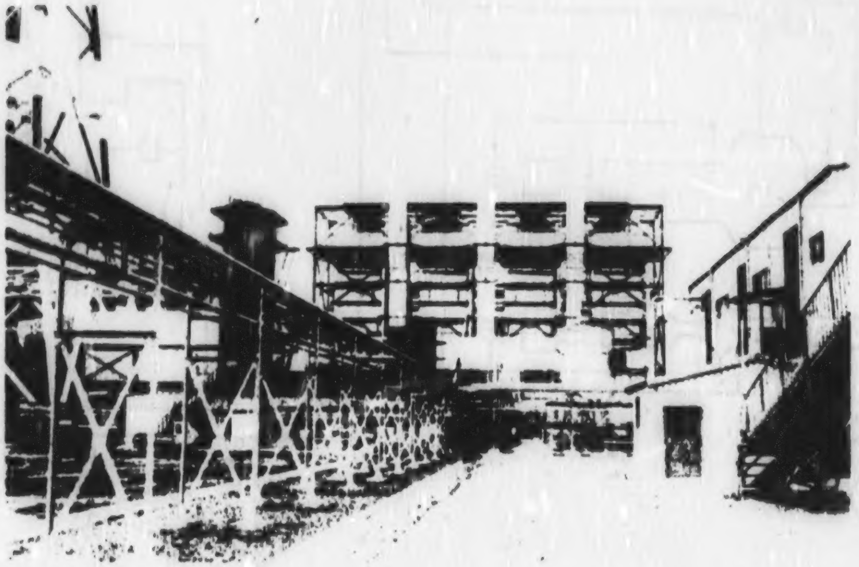


Photo 4-6. Tamashima Plant, Chugoku Electric (500 MW)

4-5, is used as the absorbent at a stoichiometry of 1.05 to 1.10. Four scrubbers were installed, of which three are in use and one is for standby. Flue gas from an oil-fired boiler, with an $SO_2$ concentration of 1,500 ppm, is first cooled to 55°C in venturi scrubbers and then led into absorbers with six stages of perforated plates, which remove about 95% of the $SO_2$.

The L/G ratio is 2.1 (liters/$Nm^3$) in the venturi and 10 in the absorber. The pH of the slurry is 5.5 in the venturi and 6 to 6.2 in the absorber. The pressure drop is fairly heavy---230 mm $H_2O$ in the venturi and 600 mm in the absorber. A calculation indicates that 99 percent $SO_2$ removal efficiency may be achieved at a total pressure drop of 1,300 ppm in the venturi and the absorber. Mist eliminators are of a new type designed by Hitachi for easy washing.

Table 4-5. COMPOSITION OF LIMESTONE

(Percent)

| | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO |
|---|---|---|---|---|---|
| Specification | >55 | <0.3 | <0.1 | <0.1 | <0.6 |
| Actual | 55 | 0.3 | 0.1 | 0.1 | 0.5 |

The calcium sulfite sludge discharged from the bottom of the venturi at pH 5.5 is sent to a reactor, where sulfuric acid is added to decompose the unreacted limestone and to lower the pH to 4.7. The slurry is sent to three oxidizers in parallel and is oxidized by air bubbles generated by rotary atomizers. More than 97 percent of the calcium sulfite is oxidized to gypsum. The gypsum contains 7 to 8 percent moisture after being centrifuged and is used in the manufacture of wallboard and cement.

## Performance

The plant came on-stream in July 1975 and has been used for base-load operation. Power consumption reaches 3.6 percent of the power generated. Small amounts of scale tend to form in some parts of the scrubber, which occasionally becomes dislodged and plugs the spray nozzles. The strainers of the circulation pumps have been improved, and operability (percentage of FGD operation hours to boiler operation hours) has reached 97 percent.

About 93 t/hr of industrial water is used, of which 13 tons are used for washing the mist eliminator. At the beginning of the operation, about 5 t/hr wastewater was purged to keep the chloride concentration of the circulating liquor below 1,000 ppm. Use of wastewater has been substantially reduced recently.

## Composition of Slurry

Solids in the slurry in the absorber circulating tank consist of calcium sulfite, 50 to 60 percent; gypsum, 40 to 50 percent; and limestone 5 percent. The relation between the pH of the slurry in the reactor (pH adjusting tank) and the composition of solids in the slurry after the oxidation is shown in Figure 4-7. When a slurry at pH 5.5 was oxidized without adding sulfuric acid, the oxidation ratio was about 80 percent. The product, consisting of about 80 percent gypsum and 20 percent calcium sulfite, has proved useful as a retarder of cement setting.

## KUREHA-KAWASAKI SODIUM-LIMESTONE PROCESS AT THE SAKAIDE PLANT, SHIKOKU ELECTRIC

### Process

The Sakaide plant went in operation in August 1975 with a capacity of treating 1,260,000 $Nm^3/hr$ of flue gas containing 1,050 ppm $SO_2$ from a 450 MW oil-fired boiler (Photos 4-7 and 4-8). The process is similar to that for Shinsendai plant, Tohoku Electric (Figure 4-8).[3] Flue gas from the 450 MW oil-fired boiler, passed through an electrostatic precipitator by a forced-draft fan, is fed into a venturi-type precooler and then into a grid-packed-type scrubber, where the gas is washed with a sodium sulfite solution (about 20%) at pH 7.0 and an L/G ratio of nearly 10 (about 70 gal/1,000 scf). The gas is then passed through a mist eliminator, reheated by an afterburner, and ducted into a stack.

The liquor discharged from the scrubber at pH 6.5 is passed through a series of five reactors, where powdered limestone, ground in a vertical tower mill to pass 325 mesh, is reacted to precipitate calcium sulfite and regenerate sodium sulfite.

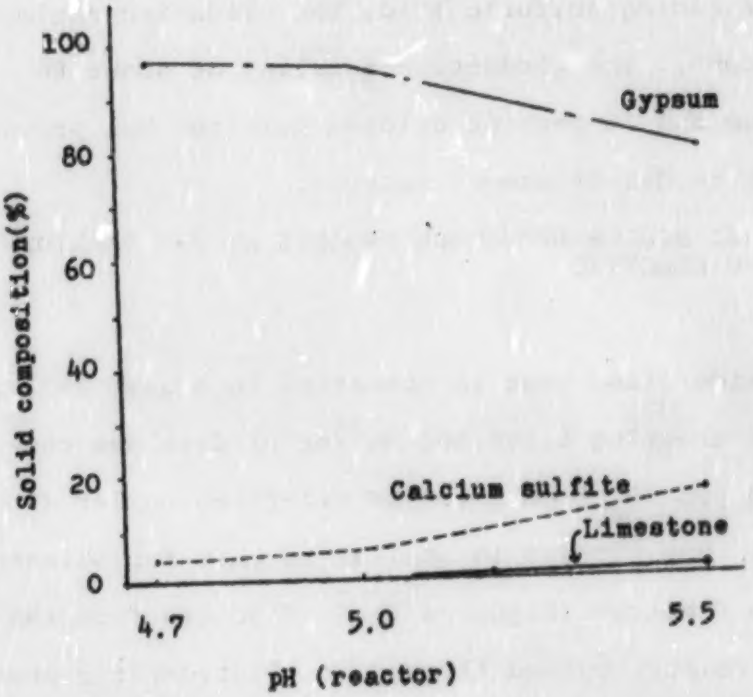


**Figure 4-7 Relationship of pH of slurry in reactor to solid composition after oxidation**

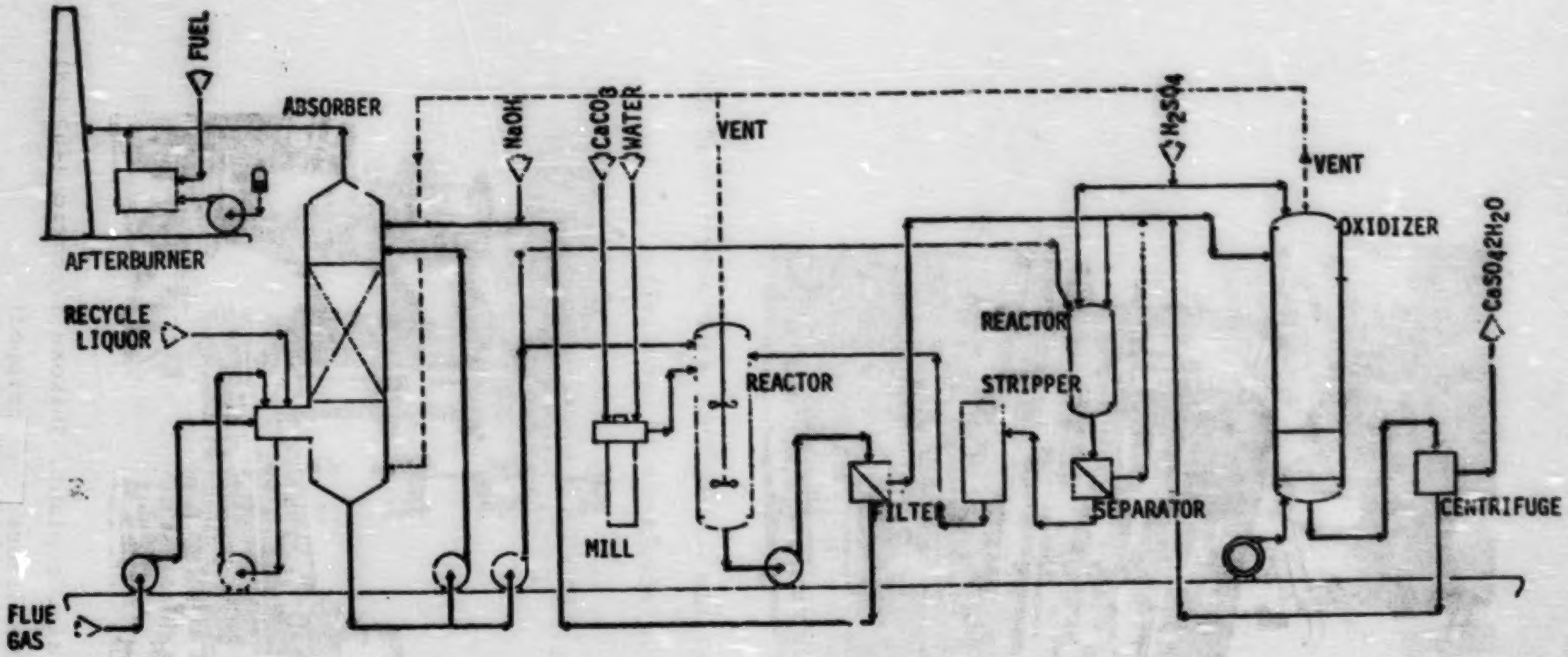

FUEL
ABSORBER
AFTERBURNER
RECYCLE LIQUOR
FLUE GAS
NaOH
$CaCO_3$
WATER
VENT
MILL
REACTOR
FILTER
$H_2SO_4$
REACTOR
STRIPPER
SEPARATOR
VENT
OXIDIZER
$CaSO_42H_2O$
CENTRIFUGE

Figure 4-8. Flowsheet of Kureha-Kawasaki process.

Photo 4-7. Sakaide plant, Shikoku Electric (450 MW)

(two scrubbers in parallel)

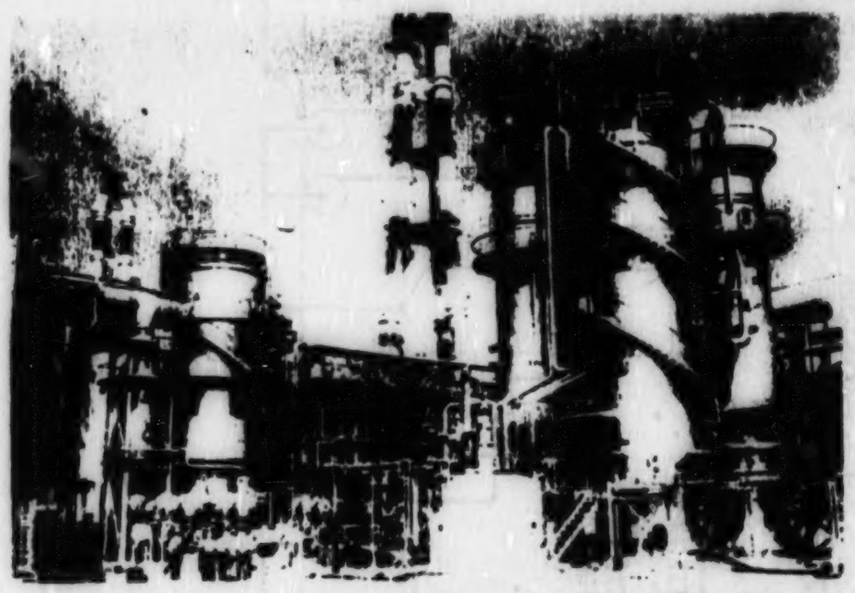


Photo 4-8. Sakaide plant, Shikoku Electric (450 MW)

(Oxidizers and stripper)

$2NaHSO_3 + CaCO_3 = Na_2SO_3 + CaSO_3 + CO_2 + H_2O$

The pH of the slurry at the outlet is 7.3. The calcium sulfite (50% slurry) is separated on a vacuum filter and washed to remove sodium sulfite. The filter cake (about 60% water) is repulped to 10 percent slurry, treated with sulfuric acid to reduce pH, and oxidized by air bubbles in an oxidizer (at 2 atmospheres of pressure) developed by Kureha and Kawasaki. The gypsum slurry is centrifuged to less than 8 percent moisture; the separated liquid is recycled to repulp the calcium sulfite.

A portion of sodium sulfite is oxidized to sulfate in the scrubber by oxygen in the flue gas. A side stream of liquor from the scrubber is treated to decompose the sulfate by reaction with sulfuric acid and calcium sulfite.

$Na_2SO_4 + 2CaSO_3 + H_2SO_4 + 4H_2O = 2(CaSO_4 \cdot 2H_2O) + 2NaHSO_3$

The slurry from the desulfation unit is filtered, and the gypsum is sent to the oxidizer as seed to obtain well-grown gypsum crystals; the separated sodium bisulfite solution is passed through a steam-heated stripper to generate $SO_2$, which is recycled to the desulfation step to reduce sulfuric acid consumption and then sent to the reactor.

A main difference from the Shinsendai plant is that the Sakaide plant incorporates a unit to remove magnesium from the circulating liquor. Magnesium derived from limestone tends to accumulate in the circulating liquor and delay the reaction of limestone with sodium bisulfite. A portion of the liquor from the gypsum centrifuge is reacted with sodium sulfite solution from the stripper to precipitate magnesium sulfite, which is filtered off. The filtrate is mixed with the liquor discharged from the scrubber.

$$MgSO_4 + Na_2SO_3 + 6H_2O \rightarrow Mg_2SO_3 \cdot 6H_2O + Ha_2SO_4$$

Another difference in the two plant operations is that here the gypsum is washed with water to reduce the sodium content as needed for use in wallboard production.

### Performance[8]

Operation parameters are shown in Table 3-5. More than 99 percent of the $SO_2$ is removed by sodium sulfite scrubbing. Operation has been smooth since start-up. The load fluctuates daily between 1,260,000 and 534,000 $Nm^3$/hr. The sodium sulfate concentration of the circulating liquor has reached 11 to 12 percent, exceeding the design value of 8 percent, but a high $SO_2$ recovery ratio has been attained. This unit is characterized by the absence of water purging from the system. At full-load operation, 63.5 t/hr water is charged, of which 29.9 tons is used for gypsum wash. The same amount, 63.5 tons, leaves the system, of which 62.0 tons is evaporated and the rest is contained in the by-product gypsum. Chloride concentration of the circulating liquor has reached 3,500 ppm but has caused no corrosion problem because the liquor contains little oxygen, which tends to cause stress corrosion in the presence of excess chloride. In the Kureha-Kawasaki process, oxidation is carried out with the calcium sulfite separated from the mother liquor, and therefore the oxygen content of the liquor is kept low. The chloride input from fuel and water and the output with gypsum containing 7 to 9 percent moisture appear to have equalized at the 3,500 ppm concentration level.

## CHIYODA PROCESS AT THE FUKUI PLANT, HOKURIKU ELECTRIC

### Process Description

A flowsheet of the Chiyoda process is shown in Figure 4-9. Flue gas is first treated by a prescrubber to eliminate dust and to cool the gas to 50°C. The cooled gas is led into a packed tower absorber containing 2-inch Tellerette. Dilute sulfuric acid (2 to 5% $H_2SO_4$), which contains ferric ion as a catalyst and is nearly saturated with oxygen, is fed to the packed tower. About 90 percent of the $SO_2$ is absorbed and partly oxidized into sulfuric acid.

The product acid is led to the oxidizing tower, into which air is bubbled from the bottom to complete the oxidation. Most of the acid at 50 to 60°C, saturated with oxygen, is returned to the absorber. Part of the acid is treated with powdered limestone (74% under 200 mesh) to produce gypsum. A special type of crystallizer has been

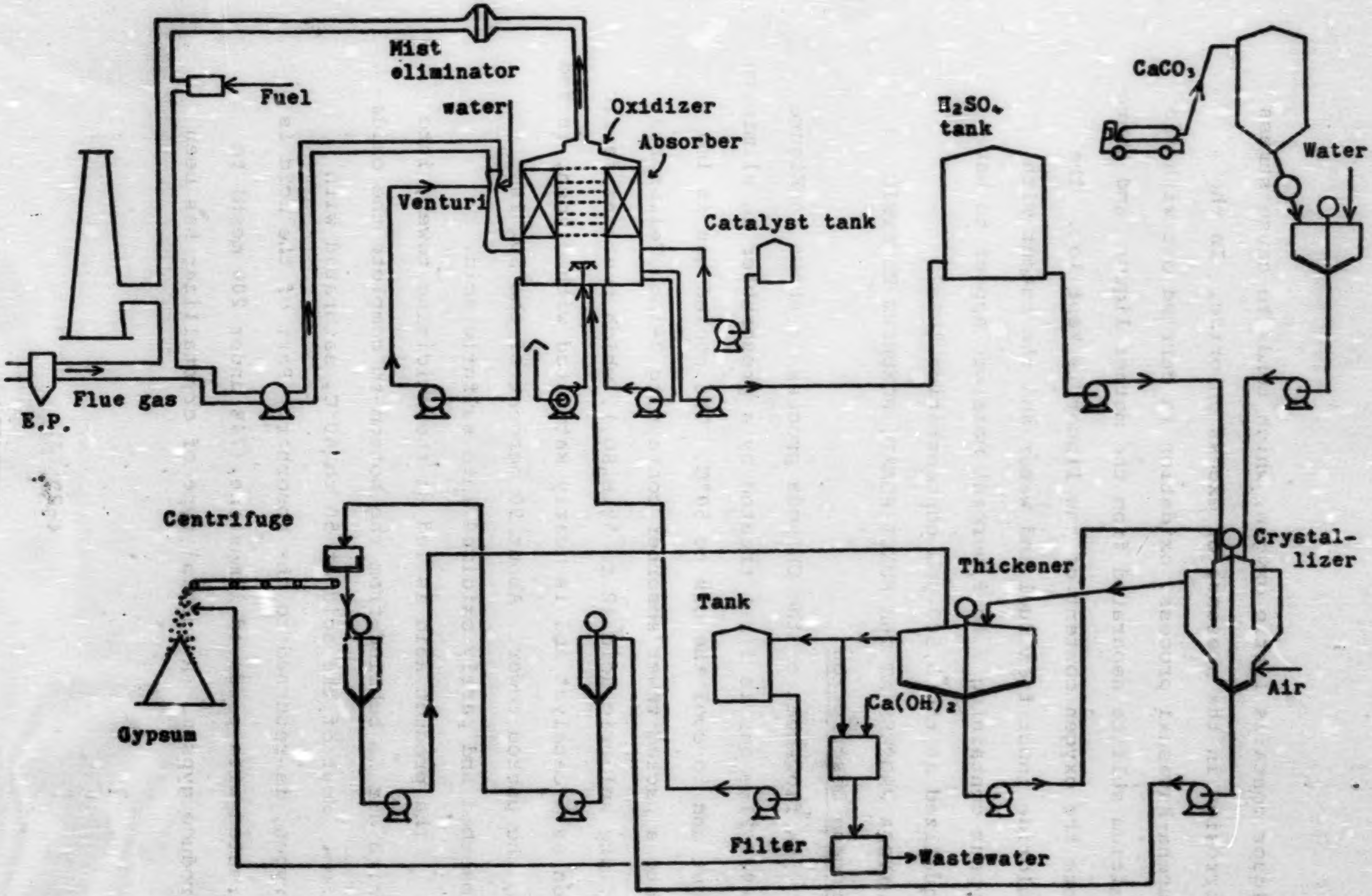

Mist eliminator
Fuel
water
Oxidizer
Absorber
Venturi
Catalyst tank
$H_2SO_4$ tank
$CaCO_3$
Water
Flue gas
E.P.
Centrifuge
Thickener
Crystal-lizer
Tank
Air
$Ca(OH)_2$
Gypsum
Filter
Wastewater

Figure 4-9. Flowsheet of Chiyoda process.

developed to obtain good gypsum with crystals ranging from 100 to 500 microns. The gypsum is centrifuged from the mother liquor and washed with water. The product gypsum is of good quality and salable.

The mother liquor and wash water are sent to the scrubber. A small amount of wastewater is discharged in order to prevent corrosion caused by the accumulation of chloride in the circulating liquor.

Performance

The Fukui plant (Photos 4-9 and 4-10) has operated smoothly since its start-up in the summer of 1975, treating 1,050,000 $Nm^3$/hr of flue gas from a 350 MW oil-fired boiler. The plant has a double-cylinder-type absorber-oxidizer. Operating parameters are listed in Table 3-5. The requirements are 150 t/day of limestone, 3.8 $m^3$/hr of oil for reheating, 11.8 MW of electric power, and 2,000 t/day of industrial water. About 580 t/day of wastewater is purged after being treated to keep the pH at 7.9, suspended solids below 5 mg/liter, and COD below 10 mg/liter. Plant operation requires only two operators per shift.

Photo 4-9. Fukui plant, Hokuriku Electric (350 MW)

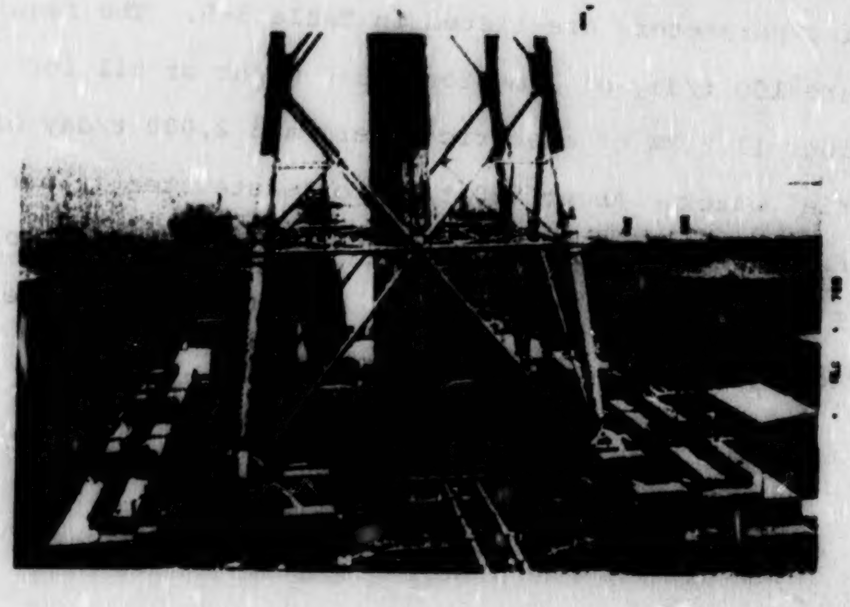


Photo 4-10. Fukui plant, Hokuriku Electric (350 MW)

## 5. FLUE GAS DESULFURIZATION IN THE STEEL INDUSTRY

### INTRODUCTION

Many desulfurization units have been installed since 1971 to treat flue gas from iron-ore sintering plants, which constitute the major source of $SO_2$ emissions in the steel industry (Table 5-1). As the absorbent, a lime slurry is used by Kawasaki Steel (MHI process), a limestone slurry by Sumitomo Metal (Sumitomo-Fujikasui Moretana process), slurry of pulverized converter slag by Nippon Steel (SSD process), and a calcium chloride solution dissolving lime by Kobe Steel (Cal process). All of these systems by-produce gypsum. Nippon Kokan uses ammonia scrubbing to by-produce ammonium sulfate or gypsum by reacting lime with the sulfate.[2]

By 1977, 22 FGD systems will be in operation, with a total capacity of treating 13,800,000 $Nm^3$/hr (8,120,000 scfm) of flue gas, which is about half the total gas from all sintering plants in Japan.

Flue gas from sintering plants is characterized by a high $O_2$ concentration (12 to 16%), a relatively low $SO_2$ concentration (200 to 1,000 ppm), and a dust rich in ferric oxide. Oxidation of sulfite into sulfate occurs in the scrubbers much more readily than with flue gas from a boiler, Table 5-1. $SO_2$ REMOVAL INSTALLATION FOR WASTE GAS FROM IRON-ORE SINTERING MACHINES

| Steelmaker | Plant site | Gas treated 1,000 $Nm^3/hr$ | Process | Absorbent | Year of completion | Gypsum, t/year |
|---|---|---|---|---|---|---|
| Kawasaki Steel | Chiba | 120 | MHI | CaO | 1973 | 3,600 |
| | Chiba | 320 | MHI | CaO | 1975 | 13,200 |
| | Chiba | 650 | MHI | CaO | 1976 | 26,500 |
| | Mizushima | 750 | MHI | CaO | 1974 | 27,600 |
| | Mizushima | 900 | MHI | CaO | 1975 | 32,400 |
| | Mizushima | 750 | MHI | CaO | 1977 | 27,600 |
| Sumitomo Metal | Kashima | 880 | Moretana | $CaCO_3$ | 1975 | 32,400 |
| | Kashima | 1,000 | Moretana | $CaCO_3$ | 1976 | 40,500 |
| | Kashima | 1,000 | Moretana | $CaCO_3$ | 1977 | 40,500 |
| | Wakayama | 370 | Moretana | $CaCO_3$ | 1975 | 14,400 |
| | Kokura | 720 | Moretana | $CaCO_3$ | 1976 | 26,500 |
| Kobe Steel | Amagasaki | 175 x 2 | Cal | $Ca(OH)_2$ | 1976 | 12,600 |
| | Kobe | 375 | Cal | $Ca(OH)_2$ | 1976 | 12,600 |
| | Kakogawa | 1,000 x 2 | Cal | $Ca(OH)_2$ | 1977 | 72,000 |
| Nakayama Steel | Osaka | 375 | Cal | $Ca(OH)_2$ | 1976 | 13,500 |
| Nippon Steel | Tobata | 200 | SSD | Slag | 1974 | 7,200 |
| | Wakamatsu | 1,000 | SSD | Slag | 1976 | 32,400 |
| Nippon Kokan | Keihin | 150 | NKK | $NH_3$, CaO | 1971 | 7,200 |
| | Fukuyama | 760 | NKK | $NH_3$[a] | 1976 | 12,000[b] |
| | Ogishima | 1,230 | NKK | $NH_3$[a] | 1977 | 20,000[b] |

[a] Ammonia in coke oven gas.

[b] Ammonium sulfate.

because the oxidation is promoted by the high $O_2/SO_2$ ratio and also by the catalytic action of the ferric oxide.

This section will describe mainly the lime and limestone processes, discussing the dimensions and performance of the FGD systems.

## MHI PROCESS AT THE MIZUSHIMA PLANT, KAWASAKI STEEL

### FGD System For No. 4 Sintering Machine

Kawasaki Steel installed FGD systems first at its Chiba Works, using the lime-gypsum process developed by Mitsubishi Heavy Industries. Satisfied with operation of these systems, Kawasaki Steel introduced larger FGD systems at its Mizushima Works, where they operate four iron-ore sintering machines with a unit capacity of 8,000 to 15,000 t/day. The No. 4 machine gives 350,000 to 750,000 $Nm^3$/hr of waste gas at about 150°C containing 500 to 1,000 ppm $SO_2$ and about 13.5 percent $O_2$.

The flowsheet of the FGD system is similar to that shown in Figure 4-1. The gas is first cooled to 57°C in a cooler with water sprays and led into a plastic-grid-packed absorber, where it is treated with a lime slurry at pH 6.4 to 7.5 at an L/G ratio of 7 liters/$Nm^3$ (about 50 gallons/1,000 scf) to remove more than 90 percent of the $SO_2$. The treated gas passes through a mist eliminator, is heated to about 140°C by afterburning, and sent to a stack. A calcium sulfite slurry discharged from the absorber is acidified to pH 4 by addition of sulfuric acid, then is led into an oxidizer and oxidized into gypsum by air bubbles generated by a rotary atomizer. The gypsum slurry is sent to a thickener and then is centrifuged to less than 10 percent moisture. The by-product gypsum is sold as a retarder of cement setting. The liquor from the centrifuge is returned to the thickener; the thickener overflow is returned to the absorber after lime is added.

A portion of the circulating liquor of the cooler is neutralized with lime to recover low-grade gypsum. The liquor from the centrifuge is sent to a wastewater treatment system and reused.

As the calcium sulfite is oxidized to a considerable extent in the absorber because of high concentration of oxygen in the gas, the gypsum is recycled to the absorber as crystal seed in order to prevent scaling. An automatic system has been installed to shut down and restart the FGD unit with the sintering machine.

## Performance

The FGD system for the No. 4 machine went into operation in November 1974. Performance characteristics are shown in Figure 5-1. The gas volume fluctuated from 350,000 to 850,000 $Nm^3/hr$ and inlet $SO_2$ concentrations ranged from

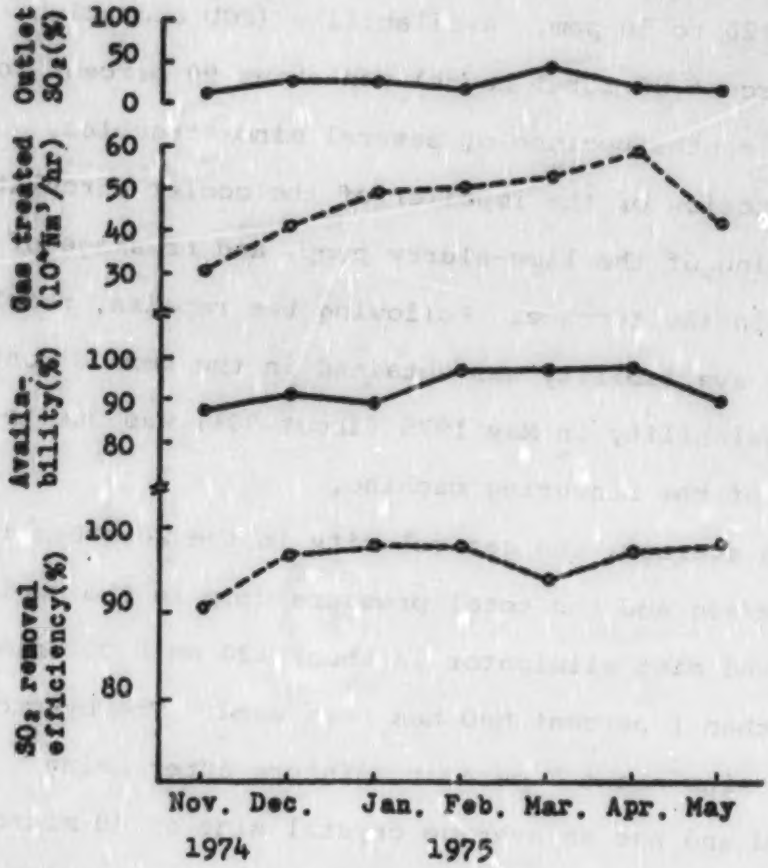


Figure 5-1. Performance of FGD plant for No. 4 sintering machine.

400 to 1,100 ppm. The $SO_2$ removal efficiency was 91 to 98 percent and the $SO_2$ concentration at scrubber outlet ranged from 20 to 50 ppm. Availability (FGD operation hours as percent of total hours) was about 90 percent for the first 3 months because of several minor troubles, such as corrosion of the impeller of the cooler circulation pump, plugging of the lime-slurry pump, and breakage of a fire-brick in the furnace. Following the repairs, nearly 100 percent availability was obtained in the next 3 months. The low availability in May 1975 (about 90%) was due to a shutdown of the sintering machine.

On the average, the gas velocity in the scrubber is about 2.5 m/sec and the total pressure drop in the cooler, absorber, and mist eliminator is about 120 mm $H_2O$. Lime with less than 1 percent MgO has been used. The by-product gypsum contains about 7 percent moisture after being centrifuged and has an average crystal size of 40 microns. At the beginning of the operation, use of an excessive amount of lime to ensure high $SO_2$ removal efficiency (over 97%) resulted in consumption of a considerable amount of sulfuric acid. In later operation, slightly less than 1 mole lime to 1 mole inlet $SO_2$ has been used to obtain about 95 percent removal, and thus the consumption of sulfuric acid has been reduced.

## FGD SYSTEMS OF SUMITOMO METAL (MORETANA PROCESS)

### Moretana Process

Sumitomo Metal is operating two FGD systems and constructing three more (Table 5-1), all using the Moretana process developed by Sumitomo jointly with Fujikasui Engineering Co. The process is characterized by use of the Moretana scrubber fitted with four perforated plates made of stainless steel. The holes range from 6 to 12 mm diameter and the plate thickness from 6 to 20 mm. Both dimensions are varied depending on the specific scrubbing conditions. Free space in the cross section ranges from 25 to 50 percent. The bottom tray serves mainly as a gas distributor, and the upper three serve as absorbers. The gas and liquid flows are adjusted to maintain a liquor head of 10 to 15 mm on each plate. Gas velocity is higher than in usual scrubbers. The design gives extreme turbulence, producing foam layers 400 to 500 mm thick, and thus ensures a high ratio of $SO_2$ and dust removal. The mist eliminator is a set of vertical chevron sections mounted in a horizontal duct after the scrubber.

A flowsheet of the process is shown in Figure 5-2. Gas from a sintering machine is first treated with water in a Moretana scrubber for cooling and removal of more than 90 percent of the dust. Removal of ferric oxide dust is useful

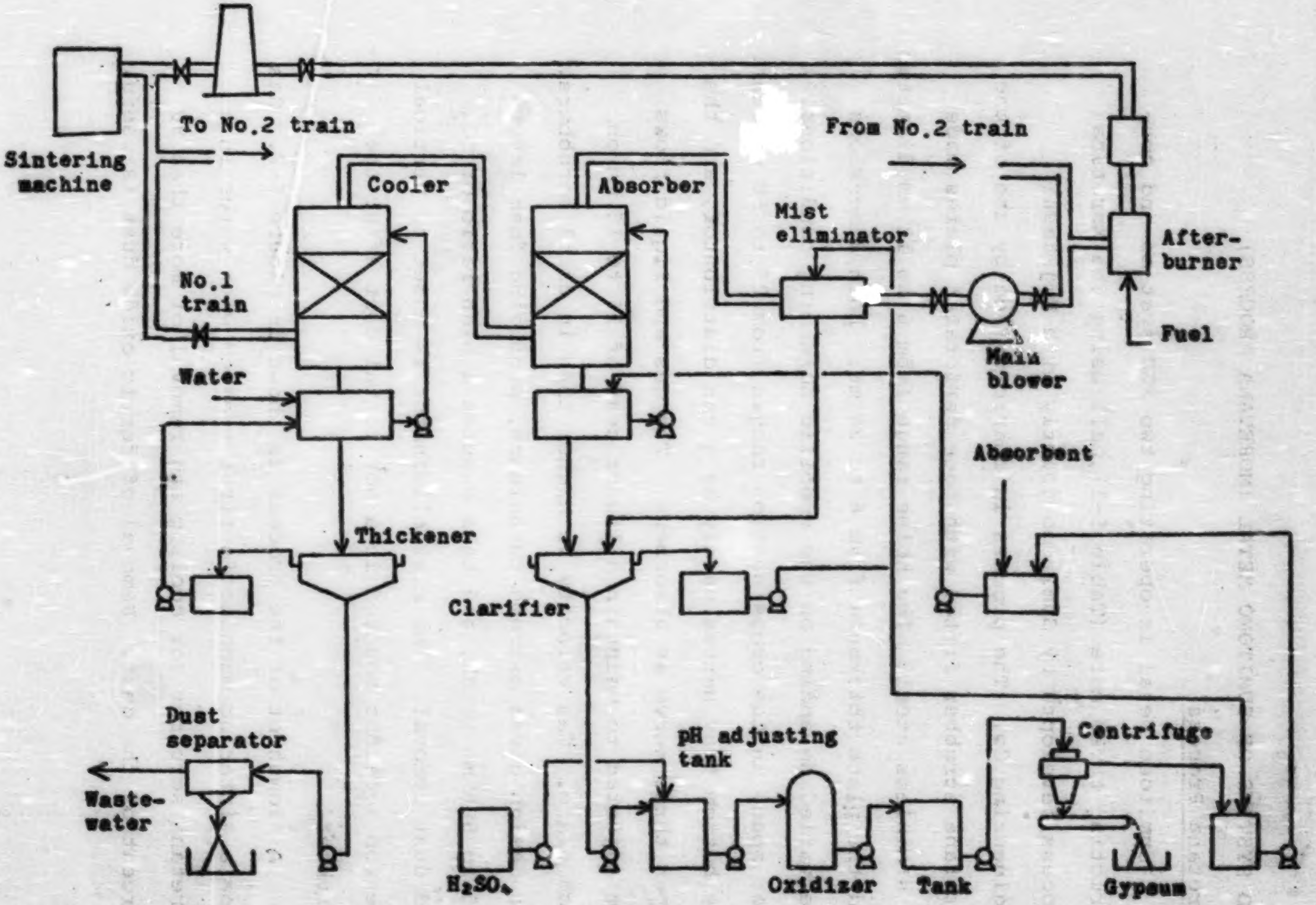

Sintering machine
To No.2 train
From No.2 train
Cooler
Absorber
Mist eliminator
After-burner
Fuel
Main blower
No.1 train
Water
Absorbent
Thickener
Clarifier
Dust separator
Waste-water
pH adjusting tank
Centrifuge
H₂SO₄
Oxidizer
Tank
Gypsum

Figure 5-2. Flowsheet of Moretana process (Kashima plant, Sumitomo Metal).

in that it reduces oxidation in the absorber to allow scale-free operation. The gas is then treated with a limestone slurry (or a mixed slurry of lime and limestone), 10 to 20 percent in excess of stoichiometric amount, in a second Moretana scrubber to remove more than 95 percent of the $SO_2$. The limestone contains less than 1 percent MgO and is ground to pass 325 mesh. The calcium sulfite slurry discharged from the scrubber is sent to a clarifier and then to a pH adjusting tank, where the pH is adjusted to about 4.0 by adding a small amount of $H_2SO_4$. The slurry is then sent to an oxidizer developed by Fujikasui to convert calcium sulfite to gypsum. The gypsum slurry is centrifuged, and the filtrate is returned to the absorber.

The discharge from the cooler is sent to a thickener. The overflow is returned to the cooler; the underflow is filtered. The filter cake is returned to the sintering machine, and the filtrate is sent to a wastewater treatment system.

Kashima Plant, Sumitomo Metal

An FGD system at the Kashima plant, with capacity of treating 880,000 $Nm^3$/hr of gas, was started up in September 1975 and has been in stable operation. All the gas from a sintering machine is treated, flow rates ranging from 350,000 to 880,000 $Nm^3$/hr. The gas contains 200 to 450 ppm $SO_2$, 14 to 15 percent $O_2$, 6 to 8 percent $CO_2$, 1 to 1.5

percent CO, 4 to 10 percent $H_2O$, and 0.15 to 0.23 g/$Nm^3$ of dust at about 150°C. The scrubbing units consist of two trains, each with a capacity of treating 440,000 $Nm^3$/hr of gas. The Moretana scrubber works normally with a gas velocity between 3 and 5 m/sec. When the gas flow rate is low, only one train is used. Equipment dimensions are shown in Table 5-2. Operational data on No. 1 train only are shown on Figure 5-3.

Table 5-2. EQUIPMENT DIMENSIONS, FGD SYSTEM
AT KASHIMA PLANT

| Facility | Number | Size (Specification) |
|---|---|---|
| Cooler | 2 | 6.5 m (dia.) 24.5 m (height) |
| Absorber | 2 | 6.5 m (dia.) 20.5 m (height) |
| Mist eliminator | 2 | 6 x 6 m, 2.4 m (length) |
| Oxidizer | 2 | 2.8 m (dia.) 5.4 m (height) |
| Centrifuge | 4 | 500 kg/hr each |

## Wakayama Plant, Sumitomo Metal

An FGD plant at Wakayama (Photo 5-1), with capacity of treating 375,000 $Nm^3$/hr of waste gas from a sintering machine, started operation in May 1975 and has since operated well except for a defect in the plastic lining of a cooler, which was found early in the operation and was repaired. Operability of the plant has been about 98 percent. A scheduled shutdown of the sintering plant normally occurs every 2

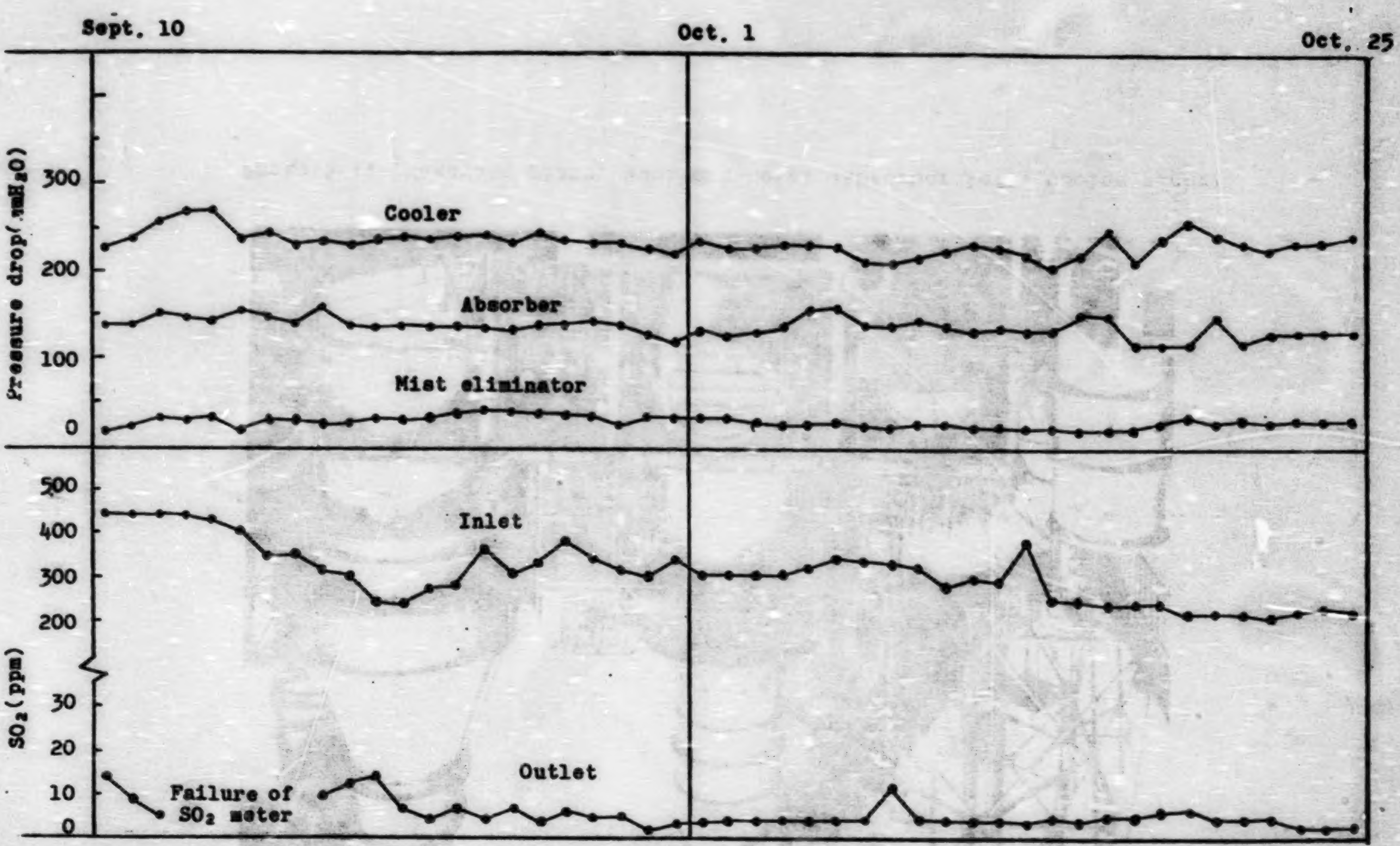


Figure 5-3. Operation data of No. 1 train, Kashima plant.

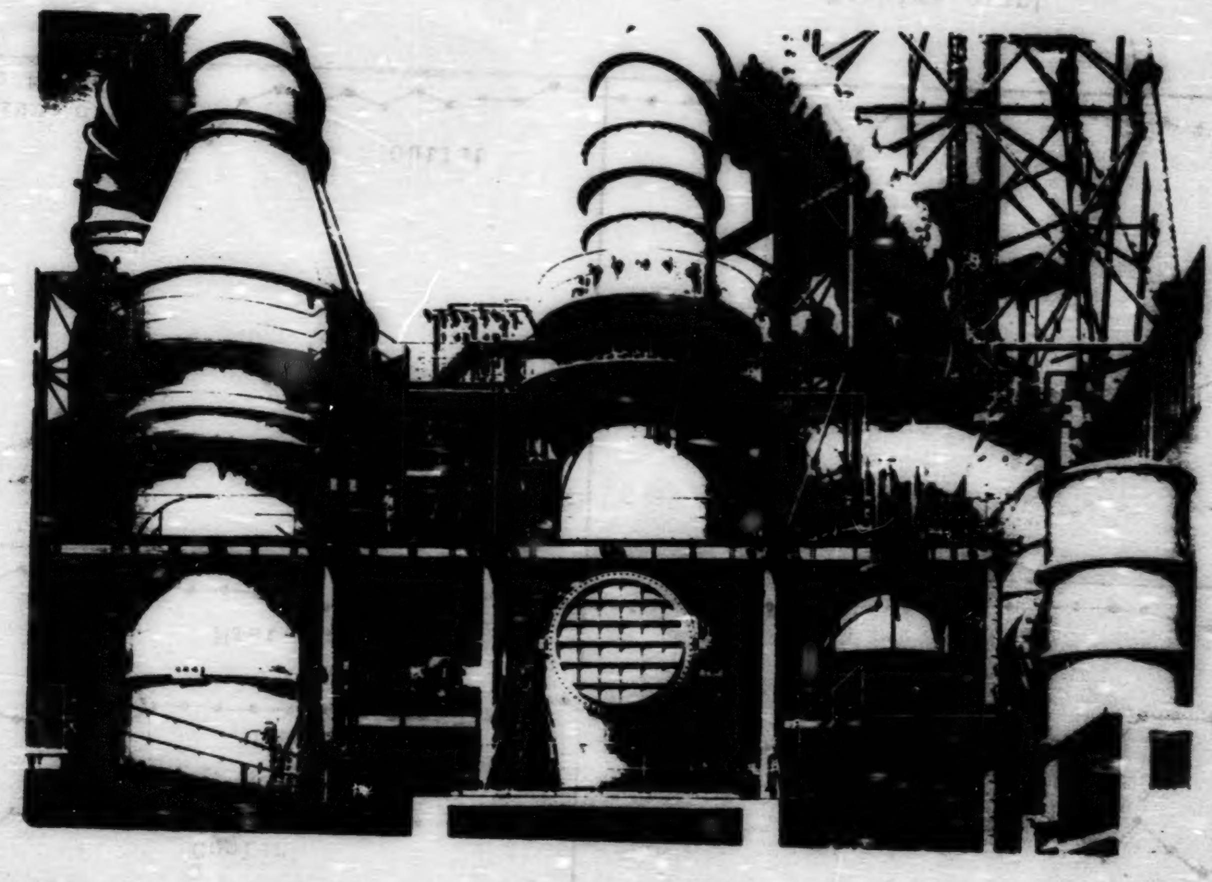


Photo 5-1. Wakayama plant, Sumitomo Metal (Absorber left, cooler right)

months. The mist eliminator is washed every 30 minutes with circulating liquor or fresh water. The pressure drop in the mist eliminator, which is 30 mm $H_2O$ at start-up, gradually increases while the unit is washed with the circulating liquor. When the pressure drop reaches 50 mm, fresh water is used in place of the liquor until the pressure drop returns to 30 mm. The ratio of liquor to fresh water usage is about 80 to 20.

## KOBE STEEL CALCIUM CHLORIDE PROCESS

### Process Description

Kobe Steel has developed a new process using a 30 percent calcium chloride solution dissolving lime as the absorbent. A pilot plant (50,000 $Nm^3$/hr) has been operated, and two commercial systems (Table 5-1) have just come on-stream to treat waste gas from iron ore sintering plants.

Calcium chloride solution dissolves 6 to 7 times as much lime as does water. High $SO_2$ recovery is attained at a low L/G ratio of 3 liters/$Nm^3$. The flowsheet is shown in Figure 5-4.

Waste gas is first cooled in a cooler to which a calcium chloride solution (about 5%, from a gypsum centrifuge) is fed to cool the gas to 70°C and to remove most of the dust. The solution is concentrated here to about 30 percent and is sent to a scrubber system after dust removal

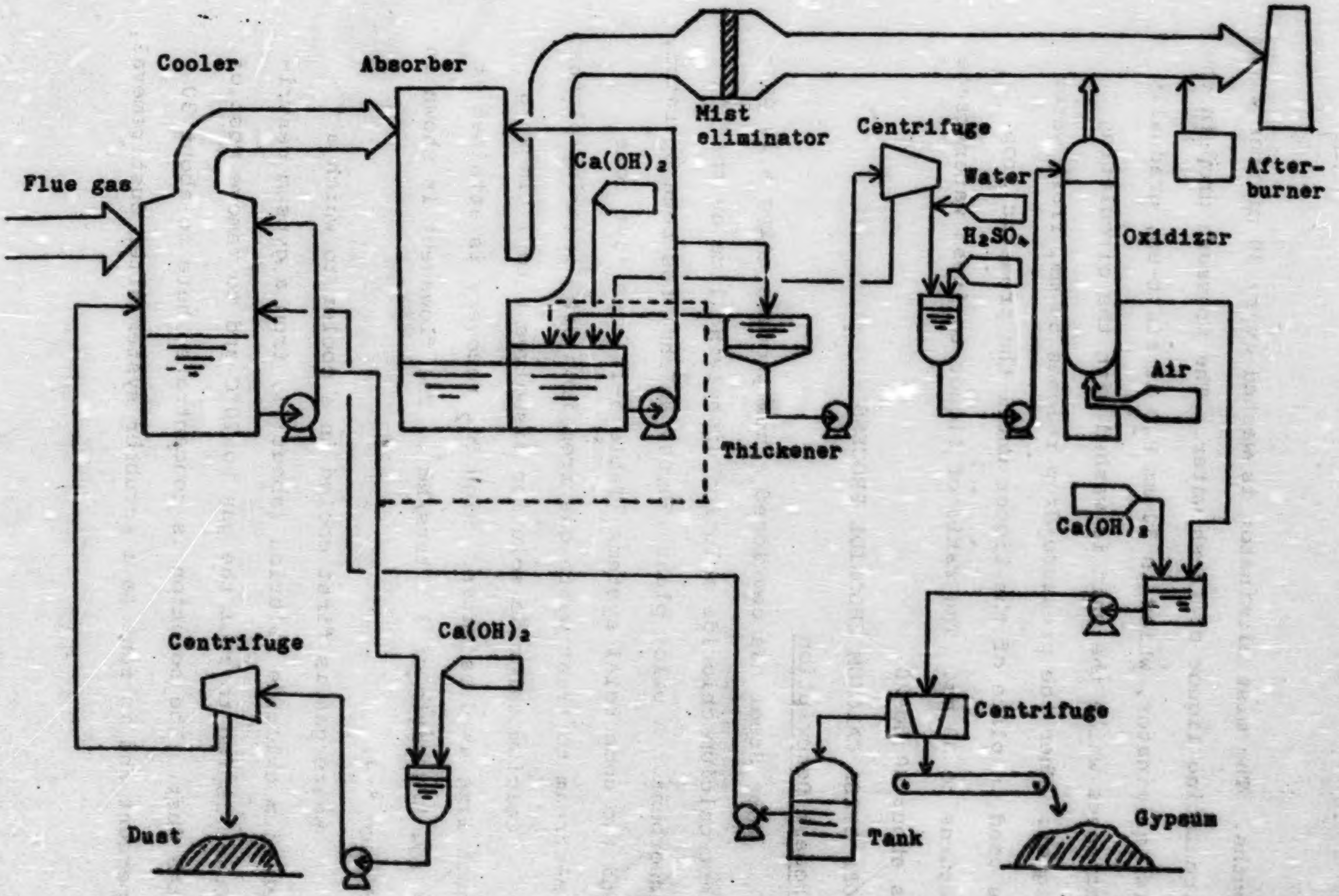

Flue gas
Cooler
Absorber
$Ca(OH)_2$
Mist eliminator
Centrifuge
Water
$H_2SO_4$
Oxidizer
After-burner
Air
Thickener
$Ca(OH)_2$
$Ca(OH)_2$
Centrifuge
Centrifuge
Tank
Gypsum
Dust

Figure 5-4. Flowsheet of Cal process.

by filtration. The gas then enters an absorber, in which a calcium chloride solution (about 30%, at pH 7 dissolving lime) is sprayed to remove more than 90 percent of the $SO_2$. The gas is then passed through a mist eliminator to a stack. The liquor discharged from the absorber at pH 5.5 containing calcium sulfite is sent through a thickener to a centrifuge to separate most of the solution, which is sent to a tank where calcium hydroxide is dissolved to raise the pH to 7. The calcium sulfite sludge from the centrifuge is repulped with water and some sulfuric acid to produce a slurry at pH 4. The slurry is oxidized by air bubbles into gypsum, which is then centrifuged. The liquor from the centrifuge, containing about 5 percent calcium chloride, is returned to the cooler. The system gives no wastewater.

Since vapor pressure of the liquor is low, the temperature of the gas after the scrubbing reaches 70°C. Thus less energy is required for reheating than in the usual wet processes with gas temperatures of 55 to 60°C at the scrubber exit. The mist eliminator is washed with the circulating liquor. The solubility of gypsum in the liquor is very low (nearly 1/100 of that in water), and evaporation of the liquor does not cause scaling.

In continuous operation of the pilot plant for about 6 months, a soft deposit formed on the wall of the absorber when the L/G ratio was less than 1; the deposit could be removed by use of an L/G ratio greater than 2. A highly corrosion-resistant material is required for the cooler; the lower part at the hot gas inlet is made of titanium.

## Amagasaki Plant

The FGD system at the Amagasaki plant has two trains, each with a capacity of treating 175,000 $Nm^3$/hr of flue gas at 120°C containing 240 to 400 ppm $SO_2$, 0.05 to 0.2 g/$Nm^3$ dust and 14 to 16 percent $O_2$. The plant began test operation in February 1976. The following problems were encountered during a 2-month test run:

Unusual vibration of a centrifuge.

Wearing of a control valve.

Scaling of pH meter electrode.

Breakage of rubber lining in a reducer.

Those problems have been solved, and the system went into commercial operation in April 1976. $SO_2$ removal efficiency ranges from 91 to 94 percent. Dust removal efficiency is about 50 percent. Gas velocity in the absorber is 3 m/sec. Total pressure drop in the cooler, absorber, and mist eliminator is 190 mm $H_2O$. The L/G ratios are 4.0 in the cooler and 3.0 in the absorber. More than 50 percent of the calcium sulfite is oxidized in the absorber. The by-product gypsum has an average crystal size of 40 microns and contains about 8 percent moisture and 0.1 percent chloride after being centrifuged.

## NIPPON STEEL SLAG PROCESS (SSD PROCESS)

Nippon Steel has developed an FGD process that uses converter slag as the absorbent (Figure 5-5). The slag contains about 40 percent CaO, 16 percent $SiO_2$, 3 percent MgO, 3 percent $Al_2O_3$, and 35 percent FeO and $Fe_2O_3$; the slag is otherwise useless. Nippon Steel has operated a prototype system with a capacity of treating 200,000 $Nm^3$/hr of waste gas from a sintering plant since 1974. A commercial unit (1,000,000 $Nm^3$/hr) has just started operation.

The process is similar to other lime/limestone-gypsum processes except that it uses no oxidizer. The gas is cooled and led into two absorbers in series to remove 95 percent of the $SO_2$. The slag is fed to the second absorber to produce a calcium sulfite slurry; the slurry then goes to the first scrubber, where it is entirely oxidized into gypsum due to a low pH and large amounts of iron compounds, which act as a catalyst. The by-product gypsum contains about 40 percent impurities and is discarded. Scaling encountered in the prototype system must be reduced to ensure long-term continuous operation. The system may be useful for steel processes that normally yield large amounts of useless slag.

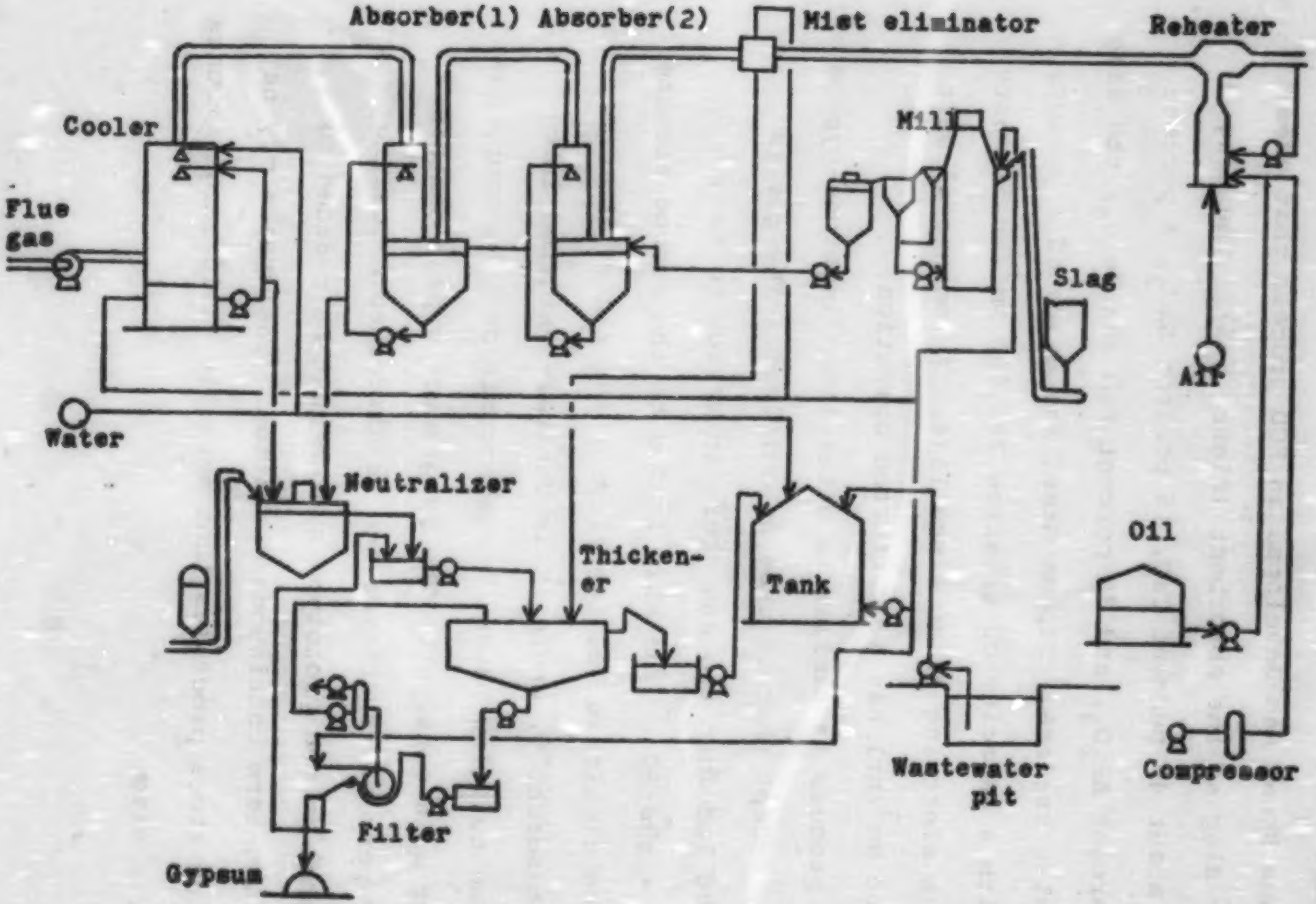

Absorber(1) Absorber(2)
Mist eliminator
Reheater
Cooler
Mill
Flue gas
Slag
Air
Water
Neutralizer
Thicken-er
Tank
Oil
Filter
Wastewater pit
Compressor
Gypsum

Figure 5-5. Flowsheet of SSD process.

## 6. NEW FGD PROCESSES

### STATUS OF NEW DEVELOPMENTS

Since 1974 several FGD systems have been newly developed in order to improve the wet lime/limestone process (Kawasaki magnesium-gypsum process and MKK jet scrubber process), to ensure stable operation at low cost (Dowa aluminum sulfate process), to attain more than 99 percent $SO_2$ removal (Kureha sodium acetate process), or to obtain as by-products elemental sulfur (Chemico-Mitsui process in combination with Claus furnace), sulfuric acid (Hitachi-Unitika activated carbon process), or ammonium sulfate (Kurabo process). These processes are described in this section.

Mitsubishi Heavy Industries and Toyo Engineering have operated pilot plants for ammonia scrubbing followed by thermal decomposition of ammonium sulfate and production of elemental sulfur using the IFP reactor. These operations may be abandoned, however, because of problems encountered, mainly in the decomposition step. A few other companies have made small-scale tests on wet processes that yield elemental sulfur, but the results have not yet been disclosed.

## KAWASAKI MAGNESIUM-GYPSUM PROCESS

### Process Description

Kawasaki Heavy Industries completed a lime-gypsum process plant in 1973. Scaling occurred in the early operations but was reduced by addition of magnesium. Recently Kawasaki constructed two commercial plants using a magnesium-gypsum process, both of which went into operation in January 1976. A flowsheet of the process is shown in Figure 6-1. Flue gas is treated in a multi-venturi type scrubber with a slurry containing calcium and magnesium sulfites. More than 90 percent of the $SO_2$ is absorbed to form bisulfites. A portion of the sulfite-bisulfite slurry is sent to an oxidizer and oxidized by air bubbling to produce gypsum and magnesium sulfate.

The gypsum slurry is treated in a thickener and then centrifuged. The filtrate is returned to the thickener. Most of the thickener overflow, containing about 5 percent magnesium sulfate, is returned to the absorber. A portion of the overflow is sent to a reactor and reacted with lime to precipitate gypsum and magnesium hydroxide. The resulting slurry is sent to the absorber; gypsum in the slurry works as seed crystal.

The pH of the slurry in the scrubber ranges from 5 to 5.5, lower than that in usual lime/limestone scrubbing.

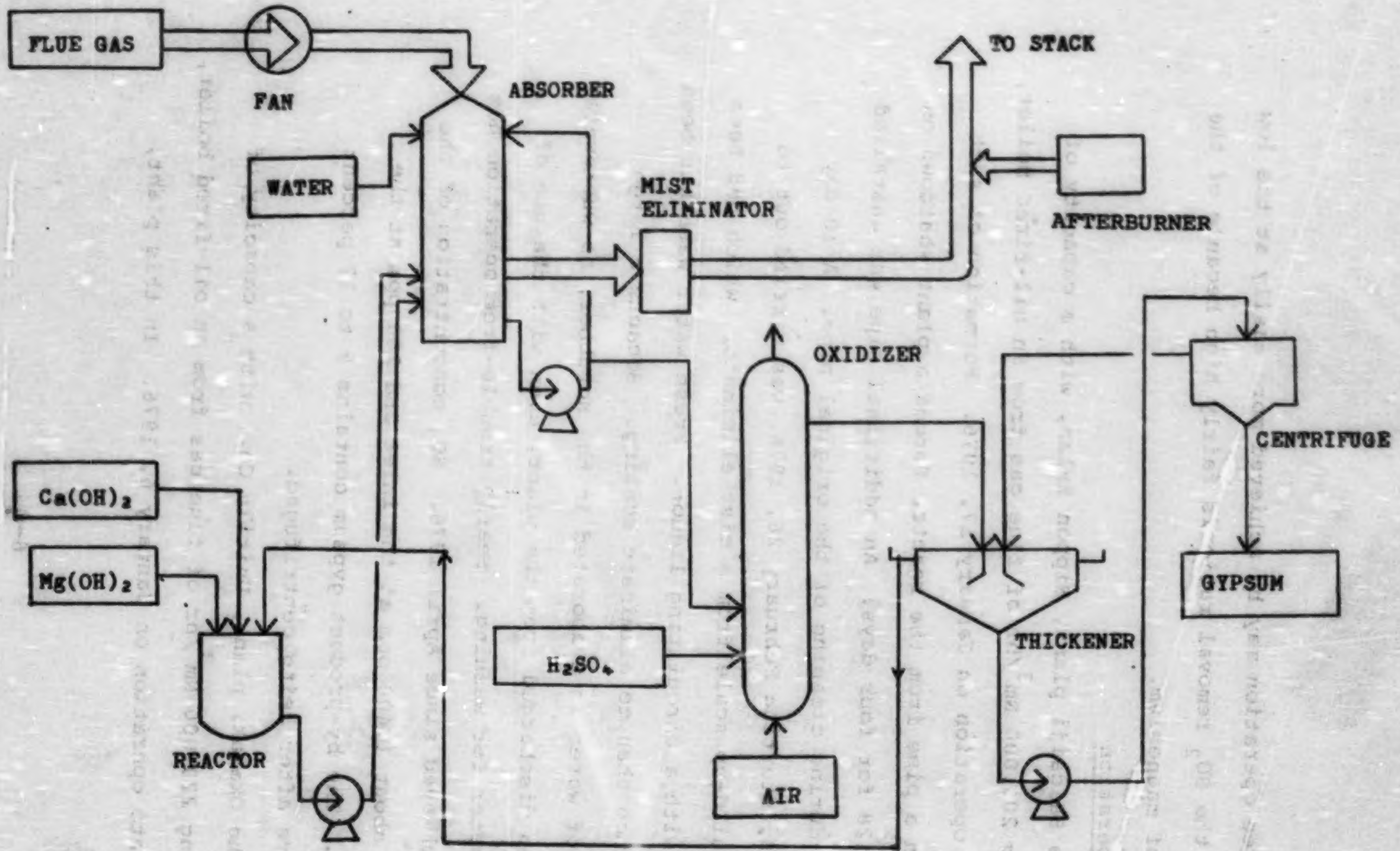

FLUE GAS
FAN
ABSORBER
TO STACK
WATER
MIST ELIMINATOR
AFTERBURNER
OXIDIZER
CENTRIFUGE
Ca(OH)₂
Mg(OH)₂
GYPSUM
H₂SO₄
THICKENER
REACTOR
AIR

Figure 6-1. Flowsheet of Kawasaki magnesium-gypsum process.

Scale-free operation may be achieved more easily at the low pH, but the $SO_2$ removal ratio is fairly high because of the effect of magnesium.

Plant Operation

The Saidaiji plant, Nippon Exlan, with a capacity of treating 200,000 $Nm^3/hr$ of flue gas from an oil-fired boiler, started operation on January 17, 1976. Formation of soft scale in a pipe from the reactor forced a plant shutdown on January 28 for four days. An additional pipe was installed for use during cleaning of the original pipe. A 10-day shutdown, starting February 26, 1976, was carried out to clean build-up scale from a mist eliminator, which had been washed with a circulating liquor. Fresh water wash has been used since then to eliminate scaling. Because a large amount of water is evaporated in the scrubber, no wastewater has been discharged from the plant, even with the use of fresh water for washing. Nearly trouble-free operation has been achieved since April 1976. $SO_2$ concentration of the gas is about 1,400 ppm at the inlet and 100 ppm at the outlet. The by-product gypsum contains 9 to 12 percent moisture after being centrifuged.

The Okazaki plant, Unitika Co., with a capacity of treating 220,000 $Nm^3/hr$ of flue gas from an oil-fired boiler, went into operation on January 6, 1976. In this plant, limestone is added to the scrubber and less lime is added to the reactor. The ratio of limestone to lime is 3.5 to 1. Problems similar to those at the Saidaiji plant were encountered at the beginning of the operation but were solved fairly easily. Operability of the plant (FGD system operating hours as a percent of boiler operating hours) from start-up until the beginning of May 1976 was 95 percent. $SO_2$ concentration is about 1,300 ppm at the inlet and 100 ppm at the outlet.

In both plants, small amounts of sulfuric acid have been added to the slurry prior to the oxidation to adjust the pH of the slurry to 5. Sulfuric acid may not be needed when the $SO_2$ concentration is over 2,000 ppm at the inlet and over 200 ppm at the outlet (as in the U.S.), because the slurry pH can be reduced to below 5 by the scrubbing. The multi-venturi scrubber has limited application. For a plant larger than 400,000 $Nm^3$/hr, Kawasaki may use the Bischoff scrubber developed in Germany.

## MKK LIME-GYPSUM PROCESS USING JET SCRUBBER

Mitsubishi Kakoki Kaisha (MKK) has constructed two lime-gypsum process systems using a screen-type scrubber. Operation is not yet completely successful. MKK recently completed a new lime-gypsum process system at Naoshima Smeltery, Mitsubishi Metal, with a capacity of treating

120,000 $Nm^3$/hr of tail gas from a sulfuric acid plant using a jet scrubber, which is a simple structure, as shown in Figure 6-2. The inside wall is kept washed with the absorbent slurry so that no scaling takes place. The tail gas, containing 1,000 to 3,500 ppm $SO_2$, is cooled in a cooler and led to the scrubber. A lime slurry is sprayed from the top by a specially designed nozzle at an L/G ratio of 12 to 15 liters/$Nm^3$; the slurry removes 90 to 95 percent of the $SO_2$. Calcium sulfite formed by the reaction is oxidized to gypsum in the scrubber by oxygen in the gas; therefore, there is no need for an oxidizer. Gypsum is centrifuged. Most of the filtrate is returned to the scrubber after lime is added. A small portion of the filtrate is sent to a wastewater treatment system together with the discharge from the cooler. The pressure drop in the scrubber is about 80 mm $H_2O$. A flowsheet of the MKK lime-gypsum jet-scrubber process installed at the Naoshima Smeltery is provided in Figure 6-3.

## DOWA ALUMINUM SULFATE PROCESS

### Process Description[9]

Dowa Mining Co. has developed an indirect limestone process using an aluminum sulfate solution at about pH 4 as the absorbent. A flowsheet of the process used at the Okayama plant, Dowa Mining, is shown in Figure 6-4. The plant has two units to treat tail gas from two sulfuric acid plants. The capacity of each unit is 150,000 $Nm^3$/hr.

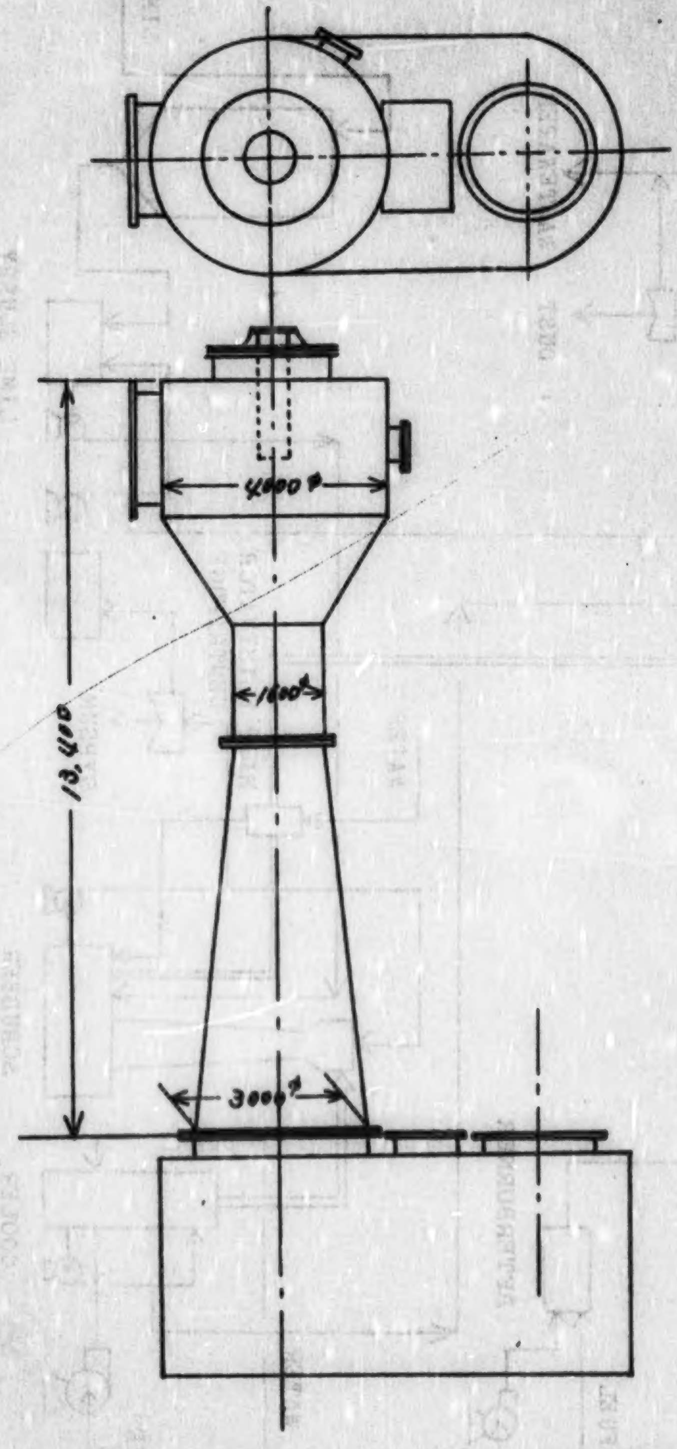

4000φ
1600φ
13,400
3000φ

Figure 6-2 Dimensions of jet scrubber(mm)
(120,000 Nm³/hr)

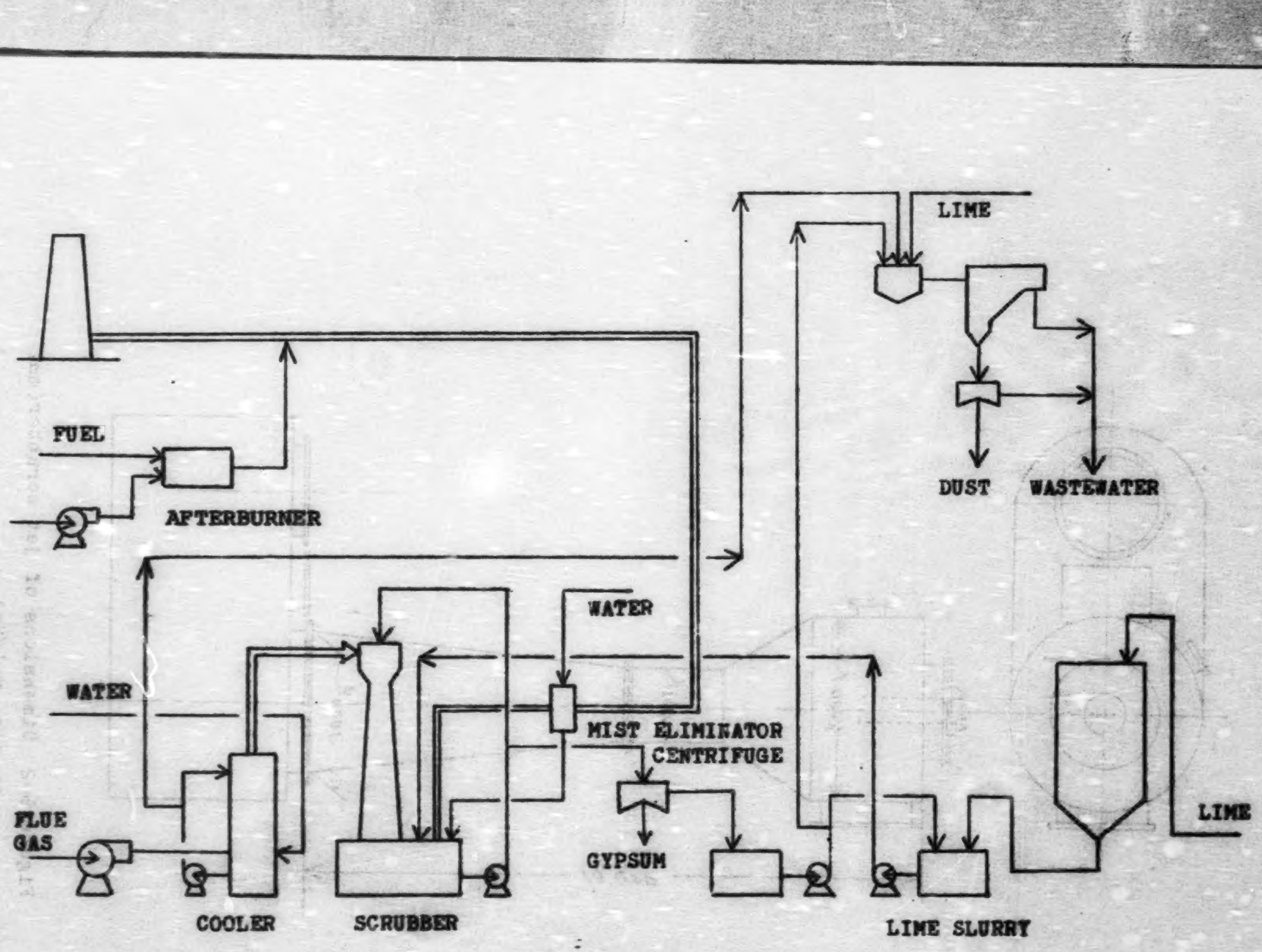

LIME
FUEL
AFTERBURNER
DUST
WASTEWATER
WATER
WATER
MIST ELIMINATOR
CENTRIFUGE
FLUE GAS
GYPSUM
LIME
COOLER
SCRUBBER
LIME SLURRY

Figure 6-3 Flowsheet of MKK jet-scrubber process (Naoshima plant)

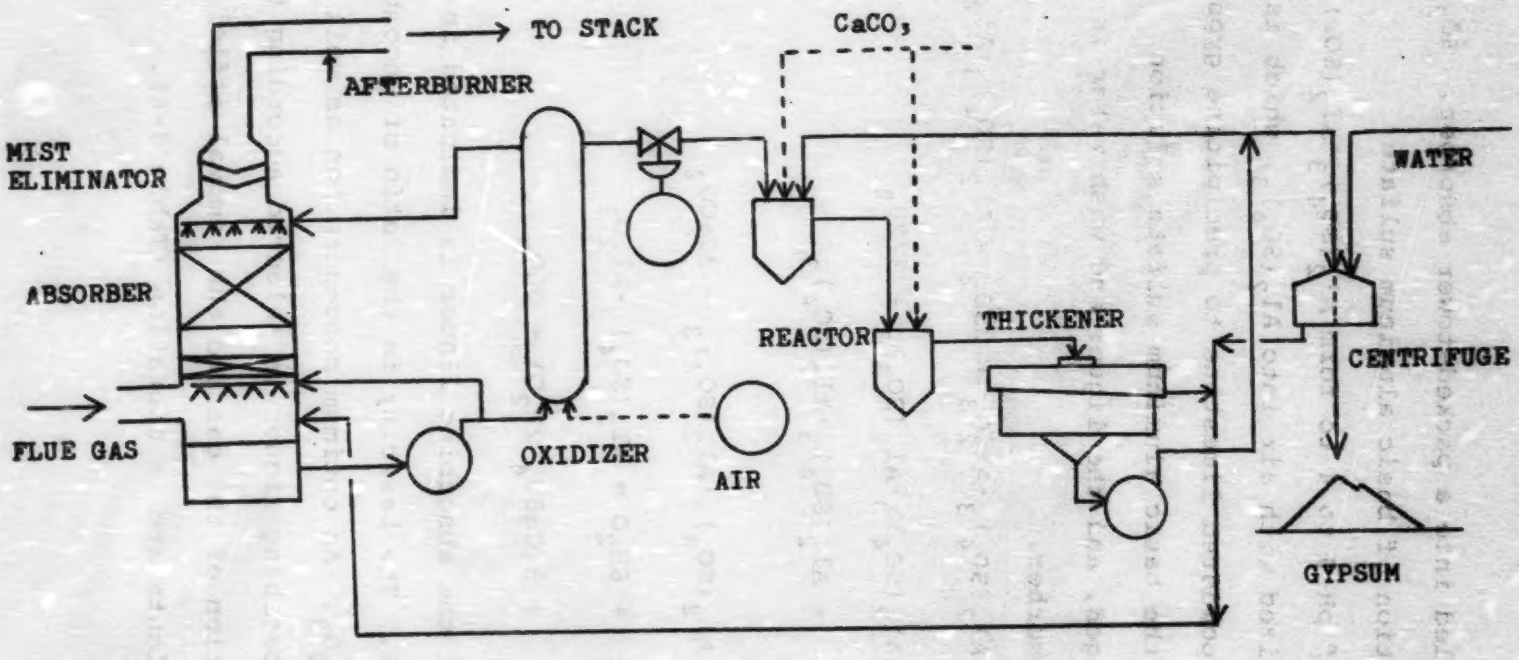

TO STACK
$CaCO_3$
AFTERBURNER
MIST ELIMINATOR
ABSORBER
FLUE GAS
OXIDIZER
AIR
REACTOR
THICKENER
WATER
CENTRIFUGE
GYPSUM

Figure 6-4 Flowsheet of Dowa aluminum sulfate-limestone process

Waste gas is led into a packed-tower absorber. $SO_2$ is absorbed in a solution of basic aluminum sulfate, $Al_2(SO_4)_3 \cdot Al_2O_3$, of pH 3 to 4 to form $Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$. The liquor is oxidized with air into $Al_2(SO_4)_3$, which is then treated with powdered limestone to precipitate gypsum and to regenerate the basic aluminum sulfate solution. The gypsum is centrifuged, and the liquor and wash water is returned to the absorber.

Absorption: $Al_2(SO_4)_3 \cdot Al_2O_3 + 3SO_2 = Al_2(SO_4)_3 \cdot Al_2(SO_3)_3$

Oxidation:
$$Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/2O_2$$
$$= Al_2(SO_4)_3 \cdot Al_2(SO_4)_3$$

Neutralization:
$$Al_2(SO_4)_3 \cdot Al_2(SO_4)_3 + 3CaCO_2$$
$$+ 6H_2O = Al_2(SO_4)_3 \cdot Al_2O_3$$
$$+ 3(CaSO_4 \cdot 2H_2O) + 3CO_2$$

The nature of the absorbing liquor is indicated in Figures 6-5 to 6-8. The basicity is the ratio of uncombined $Al_2O_3$ to total $Al_2O_3$. An optimum concentration as well as basicity of the absorbing liquor is selected according to the $SO_2$ concentration of the gas and the removal efficiency required. Four plants are in operation (Table 3-6).

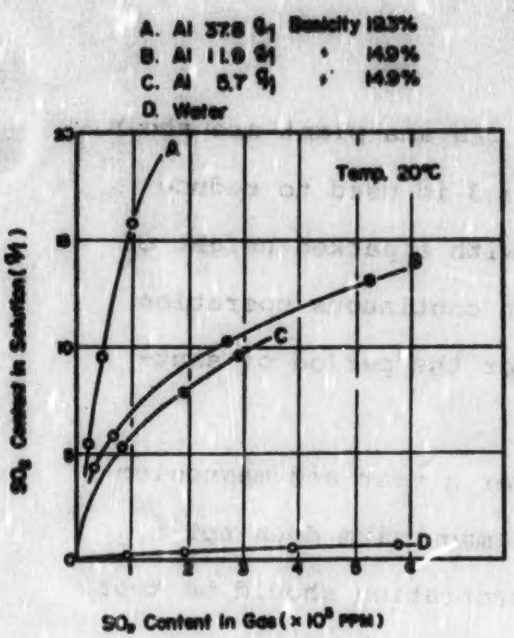


Figure 6-5 Solubility curves of $SO_2$ in BAS solutions

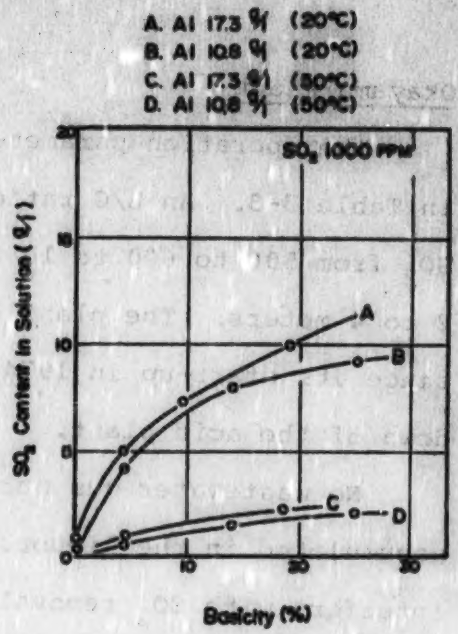


Figure 6-6 Solubility curves of $SO_2$ at various temperatures of the solution

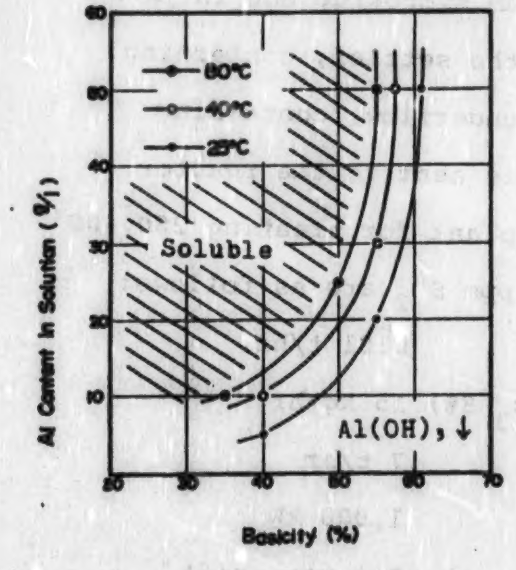


Figure 6-7 Soluble range of aluminum compound

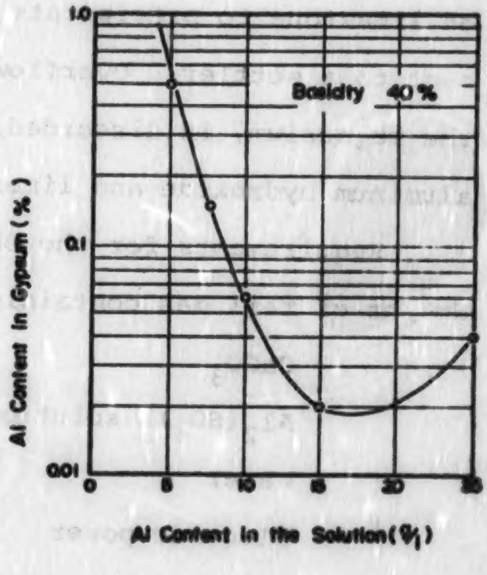


Figure 6-8 Relationship of Al loss to concentration of solution

## Okayama Plant

The operation parameters of the Okayama plant are shown in Table 3-5. An L/G ratio of 2.5 to 3 is used to reduce $SO_2$ from 500 to 600 to 10 to 20 ppm with a packed height of 2 to 4 meters. The plant has been in continuous operation since its start-up in 1974, except for the period of shutdown of the acid plant.

No wastewater was purged for over a year and magnesium accumulated in the liquor. Although magnesium does not interfere with $SO_2$ removal, its concentration should be kept below a certain level to yield good-quality gypsum for wallboard production. A small additional unit has been installed to eliminate the magnesium. A small portion of the absorbing liquor is neutralized with an excessive amount of limestone to precipitate aluminum hydroxide and is then sent to a settler. Overflow from the settler, containing the magnesium, is discarded. The underflow, containing aluminum hydroxide and limestone, is sent to the reactor.

Requirements for the Okayama plant for treating 280,000 $Nm^3$/hr of tail gas containing 650 ppm $SO_2$ are as follows:

| | |
|---|---|
| $CaCO_3$ | 0.81 t/hr |
| $Al_2(SO_4)_3$ solution ($Al_2O_3$ 8%) | 15 kg/hr |
| Water | 7 t/hr |
| Electric power | 1,000 kW |
| Operator | One per shift |

A small amount of aluminum is contained in the gypsum but this does not affect the quality of wallboard or cement produced from the gypsum. Consumption of aluminum is about 0.5 kg (as Al) for every ton of gypsum.

## Tamano Plant, Naikai Salt Production Co.

The Tamano plant, Naikai Salt Production Co., has a capacity of treating 80,000 $Nm^3/hr$ of flue gas from an oil fired boiler containing 1,500 ppm $SO_2$. This plant went into operation in March 1976 and has been in trouble-free continuous operation since then. The system has a gas cooler before the absorber. A portion of the liquor discharged from the absorber is sprayed in the cooler. It has been found that about 70 percent of the $SO_2$ is removed in the cooler. Operation data for the first month are shown in Figure 6-9.

At the beginning of operation, the $SO_2$ removal ratio ranged from 83 to 93 percent. A small amount of a soluble metallic catalyst was then added to improve the removal ratio. Since two weeks after start-up, when the gas volume increased to nearly full load and the $SO_2$ concentration to nearly 1,500 ppm, the removal ratio has been kept above 95 percent. The L/G ratio has been 10 for the scrubber. Pressure at the cooler inlet was about 100 mm $H_2O$ at full load.

No wastewater has been purged. In case of wastewater purge, the catalyst can be recovered by neutralizing the liquor.

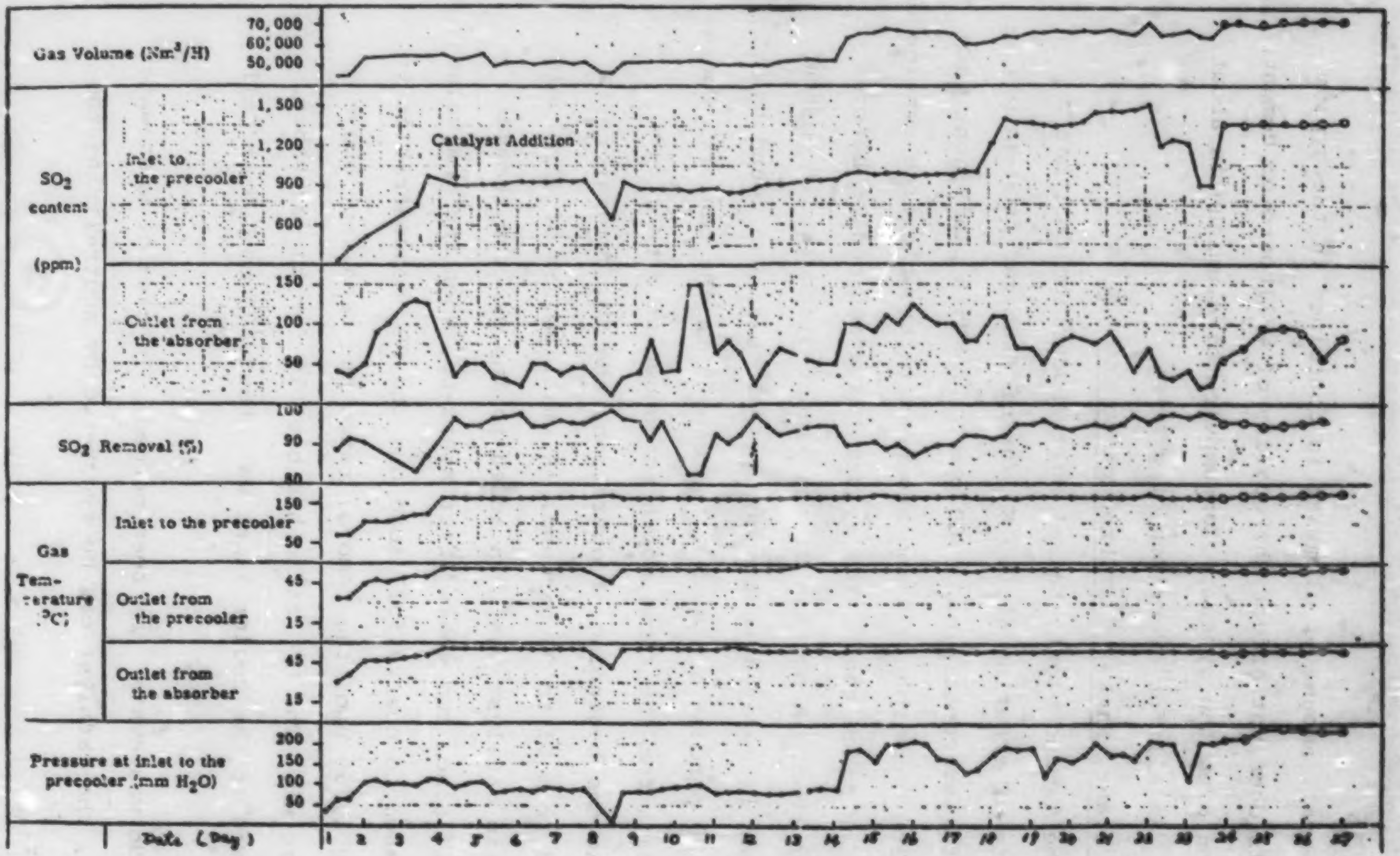


Figure 6-9. Operation data of Tamano plant, Naikai.

## KURABO AMMONIUM SULFATE-LIME PROCESS[2]

In order to prevent plume formation, which is a common problem in ammonia scrubbing, Kurabo Industries has developed a process using as the absorbent a slightly acidic ammonium sulfate solution at pH 3 to 4. Plume formation can be eliminated by the use of the acidic absorbing liquor because the vapor pressure of $NH_3$ is less than 1 ppm equivalent with a solution at a pH lower than 4. The acidic ammonium sulfate solution has a greater capacity for $SO_2$ absorption than plain water or a saturated calcium sulfate solution because of the smaller pH drop due to the following equilibrium in ammonium sulfate solution:

$$H^+ + SO_4^{--} \rightleftarrows HSO_4^-$$

A flowsheet of the process is shown in Figure 6-10. Flue gas is first led into a KBCA scrubber and then into a packed tower absorber. The main function of the KBCA scrubber is to cool the gas to 60°C and to concentrate the absorbing liquor (ammonium sulfate solution). More than 90 percent of the $SO_2$ is removed. The liquor from the packed tower absorber is sent to the KBCA unit, concentrated, and then led into an oxidizer. The pH of the liquor in the oxidizer is adjusted to 3 or 4 by adding dilute aqua ammonia; the sulfite in the liquor is oxidized to sulfate by small bubbles of air formed by introducing a jet stream of circulating liquor accompany air into a pool of the liquor.

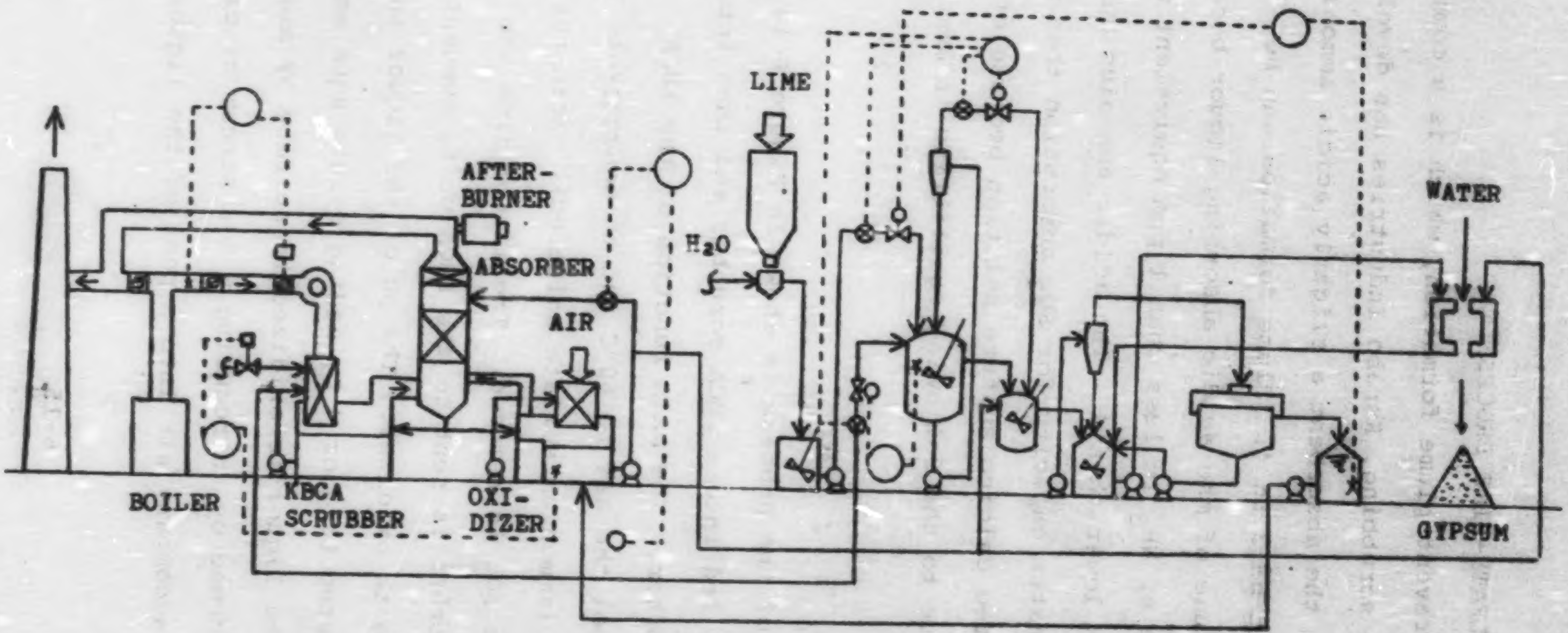

LIME
AFTER-
BURNER
ABSORBER
$H_2O$
AIR
WATER
BOILER
KBCA
SCRUBBER
OXI-
DIZER
GYPSUM

Figure 6-10 Flowsheet of Kurabo ammonium sulfate-lime process

About five times the stoichiometric amount of air is used.

Most of the liquor from the oxidizer is returned to the absorber, and a portion is sent to a set of three reactors, in which the liquor is treated with milk of lime to precipitate gypsum. The liquor from the centrifuge and the wash water are sent to an aqua ammonia tank, and the aqua ammonia is sent to the oxidizer.

Five commercial plants are in operation (Table 3-6). Operation parameters are shown in Table 3-5. The plume is almost invisible.

Ammonium sulfate solution (about 15% concentration) has been produced in the small commercial plant of Taki Chemical and used as the promoter of gypsum hardening for wallboard production. The plant has a capacity of treating 15,000 $Nm^3$/hr of flue gas containing 1,000 ppm $SO_2$ from an oil-fired boiler. More than 98 percent $SO_2$ removal has been attained with a 4.5 m packed height and an L/G ratio of about 10. The plant has been in operation since early April 1976 with 100 percent operability.

In by-production of solid ammonium sulfate, a 1.0 to 1.5 mole/liter solution may be used for absorption and concentrated in the KBCA scrubber to about a 3 mole/liter solution (nearly saturation).

## KUREHA SODIUM ACETATE PROCESS[10]

Kureha Chemical has developed an indirect lime/limestone process using a sodium acetate solution as the absorbent and has operated a pilot plant with a capacity of treating 5,000 $Nm^3$/hr of flue gas from an oil-fired boiler. The reason for the use of the acetate is to eliminate the problem of sodium sulfate, an undesirable compound that forms in sodium scrubbing processes and must be treated. In this process the acetic acid reacts with calcium to form calcium acetate, which is soluble and readily reacts with sodium sulfate to precipitate gypsum and to regenerate sodium acetate. A flowsheet of the process is shown in Figure 6-11.

$SO_2$ in flue gas is absorbed by a sodium acetate solution to form sodium bisulfite and acetic acid. Acetic acid is vaporized and caught, together with the remaining $SO_2$, by a limestone slurry at the upper part of the absorber to form a calcium acetate solution. Sodium sulfite is oxidized by air into sodium sulfate, which is then reacted with calcium acetate as mentioned above. Operation parameters are shown in Table 3-5.

Plant operation is easy, with more than 99 percent $SO_2$ recovery. Losses of acetic acid and sodium can be kept very small. On the other hand, the absorber and reactors are large, and the L/G ratio is fairly high.

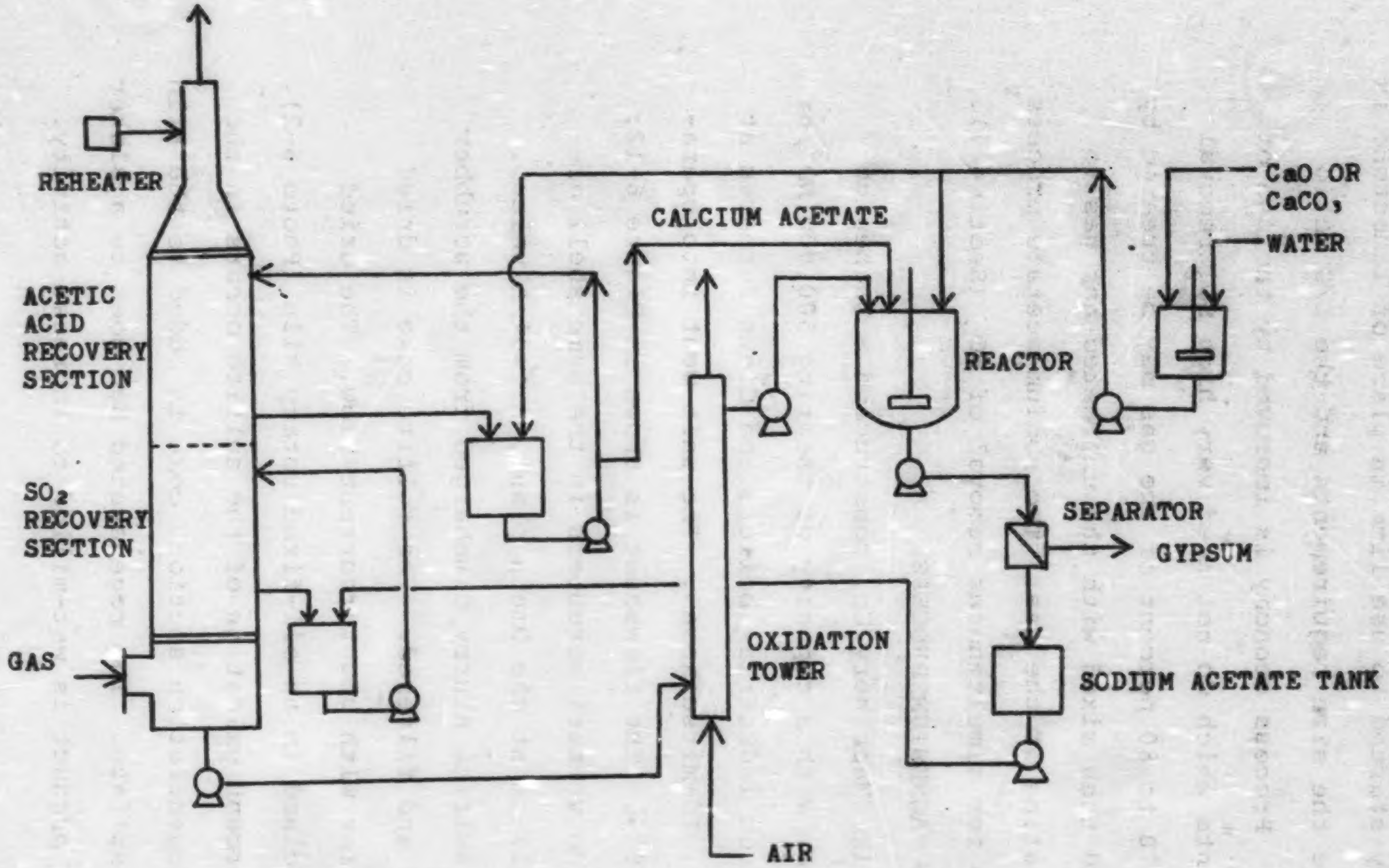

REHEATER
ACETIC ACID RECOVERY SECTION
$SO_2$ RECOVERY SECTION
GAS
CALCIUM ACETATE
CaO OR $CaCO_3$,
WATER
REACTOR
SEPARATOR
GYPSUM
OXIDATION TOWER
SODIUM ACETATE TANK
AIR

**Figure 6-11. Flowsheet of Kureha sodium acetate-lime/limestone process**

Kureha recently started to use lime in place of limestone in order to reduce the size requirements and the L/G ratio substantially. Process economy is improved by the use of lime. For plants which do not need very high $SO_2$ removal efficiencies, 70 to 80 percent of the gas may be treated by the process and then mixed with the untreated hot gas to eliminate reheating of the gas. The sodium acetate process is useful also for simultaneous removal of $NO_x$ (Section 7).

## MITSUI-CHEMICO MAGNESIUM PROCESS

Mitsui Miike Machinery Co. constructed a magnesium scrubbing system with a capacity of treating 500,000 $Nm^3/hr$ of waste gas from industrial boilers and Claus furnaces at Chiba refinery, Idemitsu Kosan. The unit went into operation in late 1974. The flowsheet is shown in Figure 6-12.

Two Chemico venturi scrubbers in the same shell are used (Photo 6-1) as at the Omuta plant, Mitsui Aluminum. The magnesium sulfite slurry discharged from the scrubber is pH-adjusted and filtered. The sulfite cake is dried in a rotary drier with countercurrent flow. The dried sulfite is calcined in an oil-fired rotary kiln (Photo 6-2). As 10 to 15 percent oxidation of the sulfite occurs in the scrubber and regeneration section, coke is added to the kiln to reduce the sulfate. The regenerated MgO goes to a slaker and the slaked product is wet-milled to increase activity.

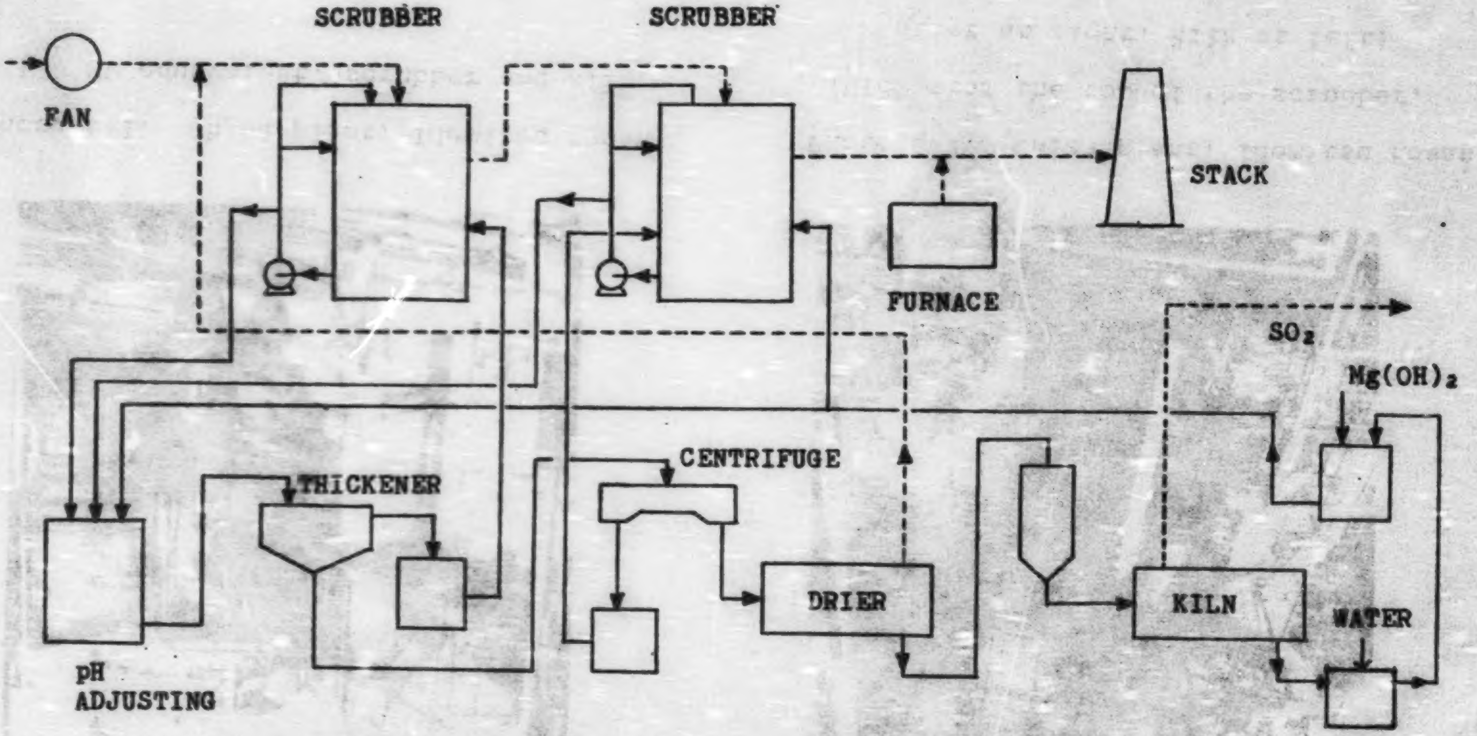

SCRUBBER
SCRUBBER
FAN
STACK
FURNACE
SO₂
Mg(OH)₂
CENTRIFUGE
THICKENER
DRIER
KILN
WATER
pH
ADJUSTING

Figure 6-12 Flowsheet of Chemico-Mitsui magnesium process

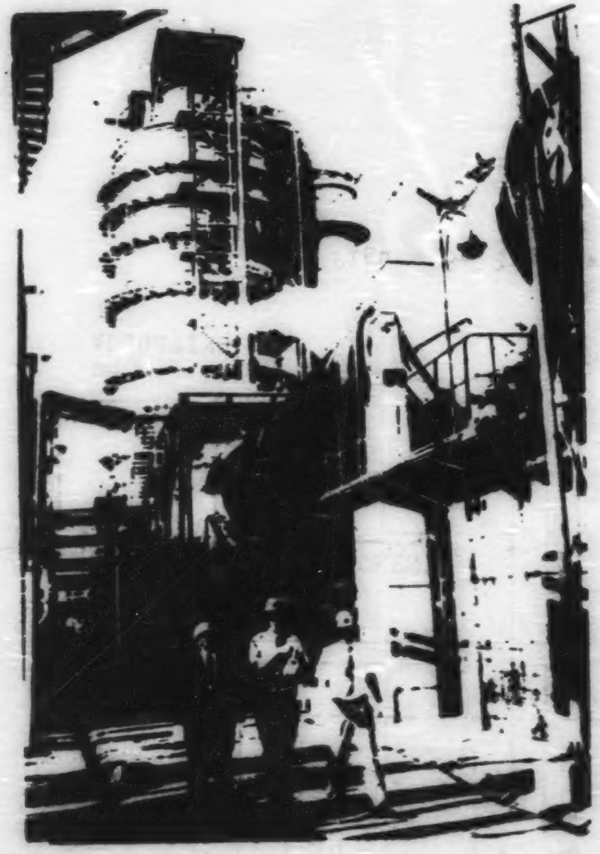


Photo 6-1. Chiba plant, Idemitsu Kosan
(170 MW equivalent, scrubber and kiln)

Photo 6-2. Chiba plant, Idemitsu Kosan
(View from the top of the scrubber,
drier at right, kiln at left)

Gas from the kiln goes through a cyclone, wet venturi, and wet precipitator. The cleaned gas containing 10 to 12 percent $SO_2$ is fed to the Claus furnace, where $H_2S$ recovered in the refinery is reacted with $SO_2$ to produce elemental sulfur. $SO_2$ concentration at the scrubber inlet is about 2,500 ppm, and the removal efficiency is 95 to 97 percent.

The form of magnesium sulfite, trihydrate or hexahydrate, is an important key to plant operation. Usually hexahydrate is preferred because it grows in much larger crystals than does trihydrate. Mitsui Miike has found that mixing the two forms gives the best results. There has been no problem with drier operation. The major problem was dislodging of the firebricks in the rotary kiln, caused possibly by the cooling of the kiln by rain. To prevent corrosion, the chloride concentration in the liquor is maintained below 2,300 ppm. Usually no wastewater is purged because the inlet chloride concentration is low.

## HITACHI-UNITIKA ACTIVATED CARBON PROCESS

Unitika Co. has installed at Uji an activated carbon process with a capacity of treating 170,000 $Nm^3$/hr of flue gas from an industrial boiler buring oil with 2.5 percent sulfur. The adsorption-desorption unit was designed by Hitachi Ltd, which had constructed a larger unit at Kashima Station, Tokyo Electric, where the dilute sulfuric acid obtained by water wash of the carbon is reacted with limestone to produce gypsum of good quality. The Kashima plant is fairly costly, but operation has been trouble-free for 3 years with virtually no loss of carbon.

At the Uji plant, Unitika, which went into operation in December 1975, dilute sulfuric acid (6 to 7 percent $H_2SO_4$) is sprayed into the incoming hot flue gas at 170°C. The gas is cooled to 80 to 90°C, and the acid is concentrated to about 60 percent. The acid is somewhat dirty and too dilute for commercial use. Unitika has used the acid in its own chemical plant and hopes to sell it locally for wastewater treatment. The acid concentration unit was designed by Unitika. There is no mist eliminator between the concentrator and the absorber. The acid mist is caught by the carbon in a fixed bed.

# 7. SIMULTANEOUS REMOVAL OF $SO_2$ AND $NO_x$

## OUTLINE

In Japan, $NO_x$ removal technology has developed rapidly since 1973, when a stringent ambient standard for $NO_2$ (0.02 ppm in daily average) was set forth. Among many processes, selective catalytic reduction of $NO_x$ by ammonia at about 400°C has been considered a most feasible means to remove 85 to 95 percent of the $NO_x$ in flue gas. Several commercial plants are treating flue gas from oil-fired industrial boilers (200,000-450,000 $Nm^3$/hr), and many plants are under construction using the reduction process.[11] This dry denitrification process, however, is not suited for use in conjunction with FGD (for which a wet process is economical), because it requires a large heat exchanger and a considerable amount of energy for heating (No. 3, Figure 7-1) or an expensive hot electrostatic precipitator (No. 4, Figure 7-1). Moreover, many existing boilers have not enough space for installation of both FGD and dentrification units. For these reasons, many dry and wet processes have been developed for simultaneous removal of $SO_2$ and $NO_x$ (No. 1 and 2, Figure 7-1), and many plants are in operation, as shown in Table 7-1.

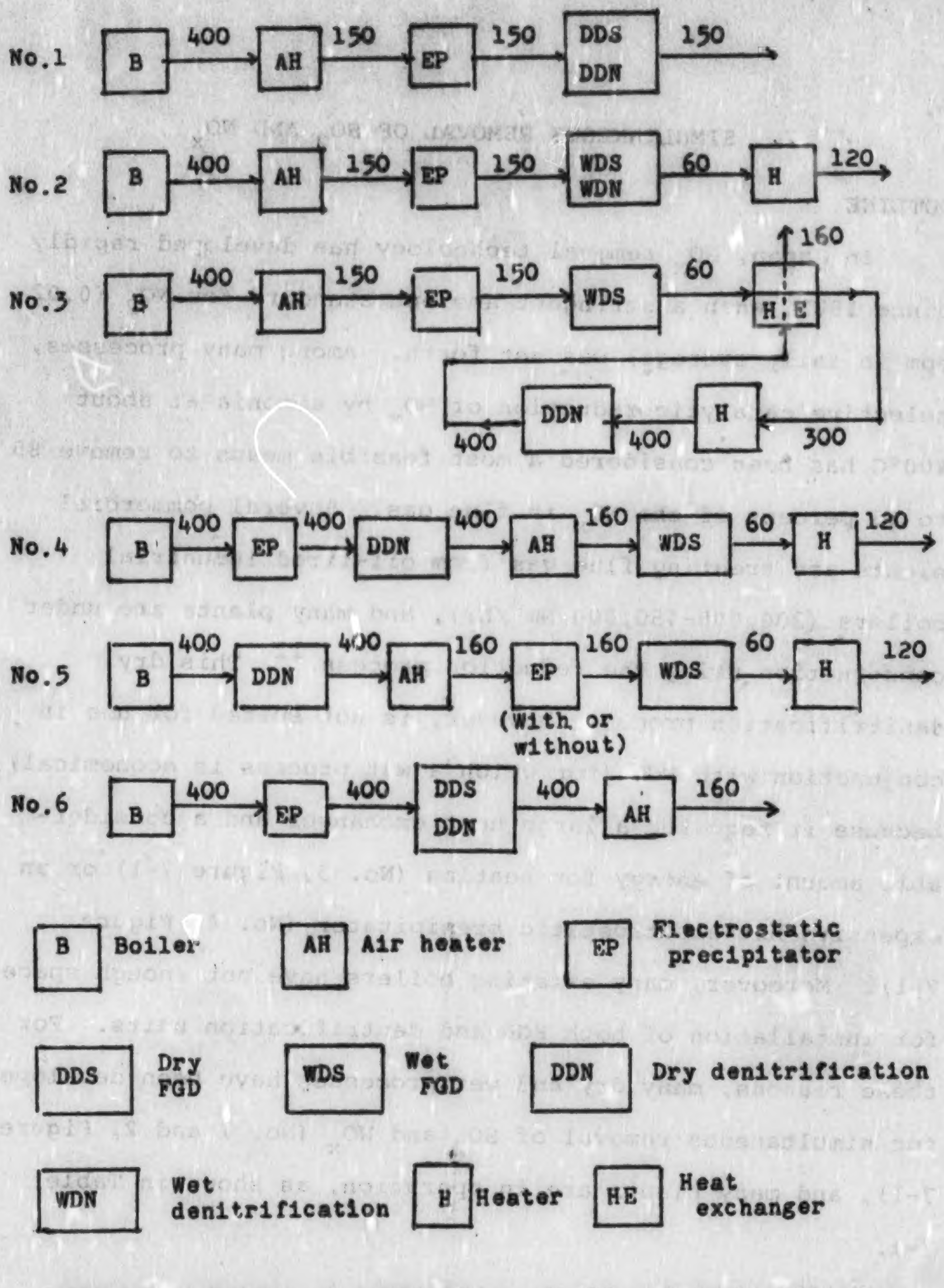

No.1
B
400
AH
150
EP
150
DDS
DDN
150
No.2
B
400
AH
150
EP
150
WDS
WDN
60
H
120
No.3
B
400
AH
150
EP
150
WDS
60
H.E
160
300
H
400
DDN
400
No.4
B
400
EP
400
DDN
400
AH
160
WDS
60
H
120
No.5
B
400
DDN
400
AH
160
EP
(With or without)
160
WDS
60
H
120
No.6
B
400
EP
400
DDS
DDN
400
AH
160
B Boiler
AH Air heater
EP Electrostatic precipitator
DDS Dry FGD
WDS Wet FGD
DDN Dry denitrification
WDN Wet denitrification
H Heater
HE Heat exchanger

**Figure 7-1 Models of combination of FGD and denitrification**
**( Figures show gas temperature)**

## Table 7-1. PROCESSES FOR SIMULTANEOUS REMOVAL OF $SO_2$ AND $NO_x$

| Process developer | Type of process | Plant owner | Plant site | Capacity, $Nm^3/hr$ | Source of gas | Completion | By-product |
|---|---|---|---|---|---|---|---|
| (Sumitomo Metal Fujikasui) | Oxidation reduction | Sumitomo Metal | Amagasaki | 62,000 | Boiler[a] | 1973 | ($NaNO_3$, NaCl, $Na_2SO_4$) |
| (Sumitomo Metal Fujikasui) | Oxidation reduction | Toshin Steel | Fuji | 100,000 | Furnace | 1974 | ($NaNO_3$, NaCl, $Na_2SO_4$) |
| (Sumitomo Metal Fujikasui) | Oxidation reduction | Sumitomo Metal | Osaka | 39,000 | Boiler[a] | 1974 | ($NaNO_3$, NaCl, $Na_2SO_4$) |
| Osaka Soda | Oxidation reduction | Osaka Soda | Amagasaki | 60,000 | Boiler[a] | 1976 | ($NaNO_3$, NaCl, $Na_2SO_4$) |
| Shirogane | Oxidation reduction | Mitsui Sugar | Kawasaki | 48,000 | Boiler[a] | 1976 | ($NaNO_3$, NaCl, $Na_2SO_4$) |
| Chiyoda | Oxidation reduction | Chiyoda | Kawasaki | 1,000 | Boiler[a] | 1973 | Gypsum, $Ca(NO_3)_2$ |
| Mitsubishi H.I. | Oxidation reduction | Mitsubishi H.I. | Hiroshima | 2,000 | Boiler[a] | 1974 | Gypsum, $NH_3$ |
| Ishikawajima H.I. | Oxidation reduction | Ishikawajima | Yokohama | 5,000 | Boiler[a] | 1975 | Gypsum, $N_2$ |
| Kureha Chemical | Reduction | Kureha Chem. | Nishiki | 5,000 | Boiler[a] | 1975 | Gypsum, $N_2$ |
| Chisso Eng. | Reduction | Chisso P.C. | Goi | 300 | Boiler[a] | 1974 | $(NH_4)_2SO_4$ |
| Mitsui S.B. | Reduction | Mitsui S.B. | Chiba | 150 | Boiler[a] | 1974 | $H_2SO_4$, $N_2$ |
| Asahi Chemical | Reduction | Asahi Chem. | Mizushima | 600 | Boiler[a] | 1974 | Gypsum, $N_2$ |
| Kawasaki H.I. | Magnesium | EPDC | Takehara | 5,000 | Boiler[b] | 1975 | Gypsum, $Mg(NO_3)_2$ |
| Unitika Co. | Carbon[c] | Union Glass | Hirakata | 5,000 | Furnace | 1975 | Conc. $SO_2$, $N_2$ |
| Sumitomo H.I. | Carbon[c] | Sumitomo Metal | Kokura | 150 | Furnace | 1975 | Conc. $SO_2$, $N_2$ |
| Shell | Copper[c] | Showa Y.S. | Yokkaichi | 120,000 | Boiler[a] | 1975 | Conc. $SO_2$, $N_2$ |
| Ebara-JAERI | Electron beam[c] | Ebara | Fujisawa | 1,000 | Boiler[a] | 1974 | Mist, dust |

[a] Oil-fired boiler.

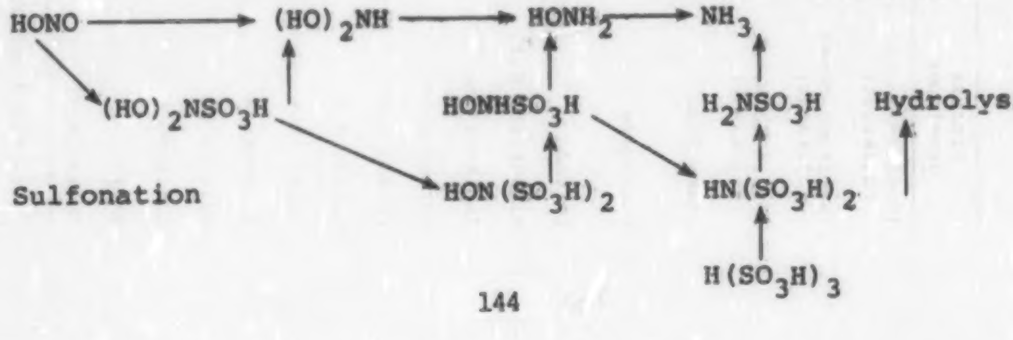
[b] Coal-fired boiler.

[c] Dry process.

## CHEMISTRY AND PROBLEMS OF WET PROCESSES

Most of the $NO_x$ in combustion gas is in the form of NO, which has little reactivity and does not readily dissolve in solutions. NO can be absorbed in a solution containing an oxidizing agent such as potassium permanganate, hydrogen peroxide, or calcium hypochlorite; an absorption oxidation process may be too expensive for commercial use on a large scale, however, particularly when the gas contains much $SO_2$, which consumes the oxidizing agent. Moreover, treatment of the by-product liquor containing a nitrate, nitrite, and sulfate will present a problem.

NO is slowly oxidized into $NO_2$ in air. Gaseous oxidizing agents, ozone and chlorine dioxide, oxidize NO very rapidly, within 1 second, but they hardly oxidize $SO_2$ into $SO_3$. Since 1972 several oxidation reduction processes have been developed in Japan, by which NO is first oxidized to $NO_2$ by the oxidizing agent and is absorbed in a solution or slurry together with $SO_2$. Various reactions occur in the solution or slurry as shown below, resulting in the reduction of $NO_x$ by $SO_2$ (or sulfite) to $N_2$ or $NH_3$.[12]



The reactions to form $N_2$ are more complex but may be described as in equation (1) or more simply as in equation (2).

$$NH_2SO_3H + NO_2^- \rightarrow N_2 + HSO_4^- + H_2O \qquad (1)$$

$$2NO_2 + 4SO_3^{--} \rightarrow N_2 + 4SO_4^{--} \qquad (2)$$

In some of the processes a considerable portion of $NO_x$ remains in the resulting liquor as a nitrite and nitrate. For a large-scale operation, it is desirable not to have those nitrogen compounds in solution because they present problems in wastewater treatment.

In addition to the oxidation reduction processes, several reduction processes have been developed using solutions containing ferrous ion and EDTA (ethylenediaminetetraacetic acid, a chelating compound whose present cost in Japan is about $2,700/t), which absorbs NO fairly well. The absorbed NO reacts with sulfite and is converted to $N_2$ or $(NH_4)_2SO_4$. Otherwise, the NO can be regenerated in a concentrated form.

The wet simultaneous processes have not yet been commercialized on a large scale; five relatively small commercial plants are in operation, as shown in Table 7-1. The major problem for the oxidation reduction processes has been the high cost of ozone ($1.2 to $1.4/kg). Although chloride dioxide is less expensive, it brings chloride into the system and complicates the process. Another problem has been the formation of considerable amounts of nitrate and nitrite in the absorbing liquor. Improvements have been made to prevent the nitrogen compounds from remaining in the liquor as well as to produce ozone at lower cost. The major problems for the reduction process have been the requirements of expensive EDTA, a large absorber, and a high L/G ratio. Efforts have been made to minimize the consumption of EDTA.

On the positive side, the wet processes offer the following advantages: (1) They are not affected by particulates in the gas as are the dry processes using a catalyst. (2) Their $NO_x$ removal efficiency exceeds 80 percent, whereas that of the ammonia injection process without catalyst may not reach 70 percent on a large scale. (3) The wet processes do not consume ammonia. Some of the processes can produce ammonia from $NO_x$. For future worldwide use, the wet processes may be practicable if the process economy can be considerably improved, because the dry processes consume large amounts of ammonia and may cause shortages of nitrogen fertilizers and foods. (4) A high $SO_2/NO_x$ ratio is favorable to the reduction of $NO_x$ to $N_2$ or $NH_3$. The wet processes may be useful for treatment of flue gas burning of high-sulfur coal.

## OXIDATION REDUCTION PROCESSES

### Fujikasui-Sumitomo Process (Moretana Process)

Fujikasui Engineering, jointly with Sumitomo Metal Industries, has developed a sodium scrubbing process for removal of $SO_2$ and $NO_x$ (Figure 7-2) and has constructed three plants (Table 7-1). Gaseous $ClO_2$ is added to the gas just before the scrubber and oxidizes NO into $NO_2$ within 0.5 second. The gas is then introduced into a Moretana scrubber and is reacted with a sodium hydroxide solution. More than 98 percent of the $SO_2$ is absorbed to produce sodium sulfite. About 90 percent of the $NO_x$ in the gas is removed. About half of the removed $NO_x$ is converted into $N_2$ by the reaction with sodium sulfite and the rest into sodium nitrate and nitrite.

Capital cost is in the range of \$60 to \$90/kW. Operating cost including depreciation (7 years) is roughly \$32/kl oil or 7 mil/kWh.

The liquor from the scrubber, which contains sodium sulfate, chloride, nitrate, and nitrite, is concentrated to separate most of the sodium sulfate in a crystal form. The remaining liquor is sent to a wastewater treatment system.

Fujikasui recently started tests on ozone oxidation followed by lime scrubbing to reduce $NO_x$ to $N_2$ or $NH_3$ and to by-produce gypsum.

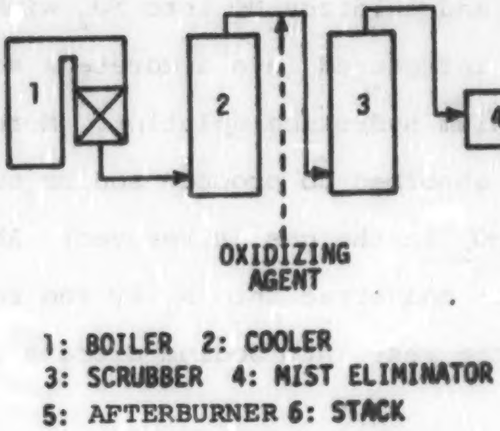

1
2
3
4
5
6
OXIDIZING AGENT
1: BOILER 2: COOLER
3: SCRUBBER 4: MIST ELIMINATOR
5: AFTERBURNER 6: STACK

Figure 7-2. Simplified flowsheet of Moretana simultaneous removal process.

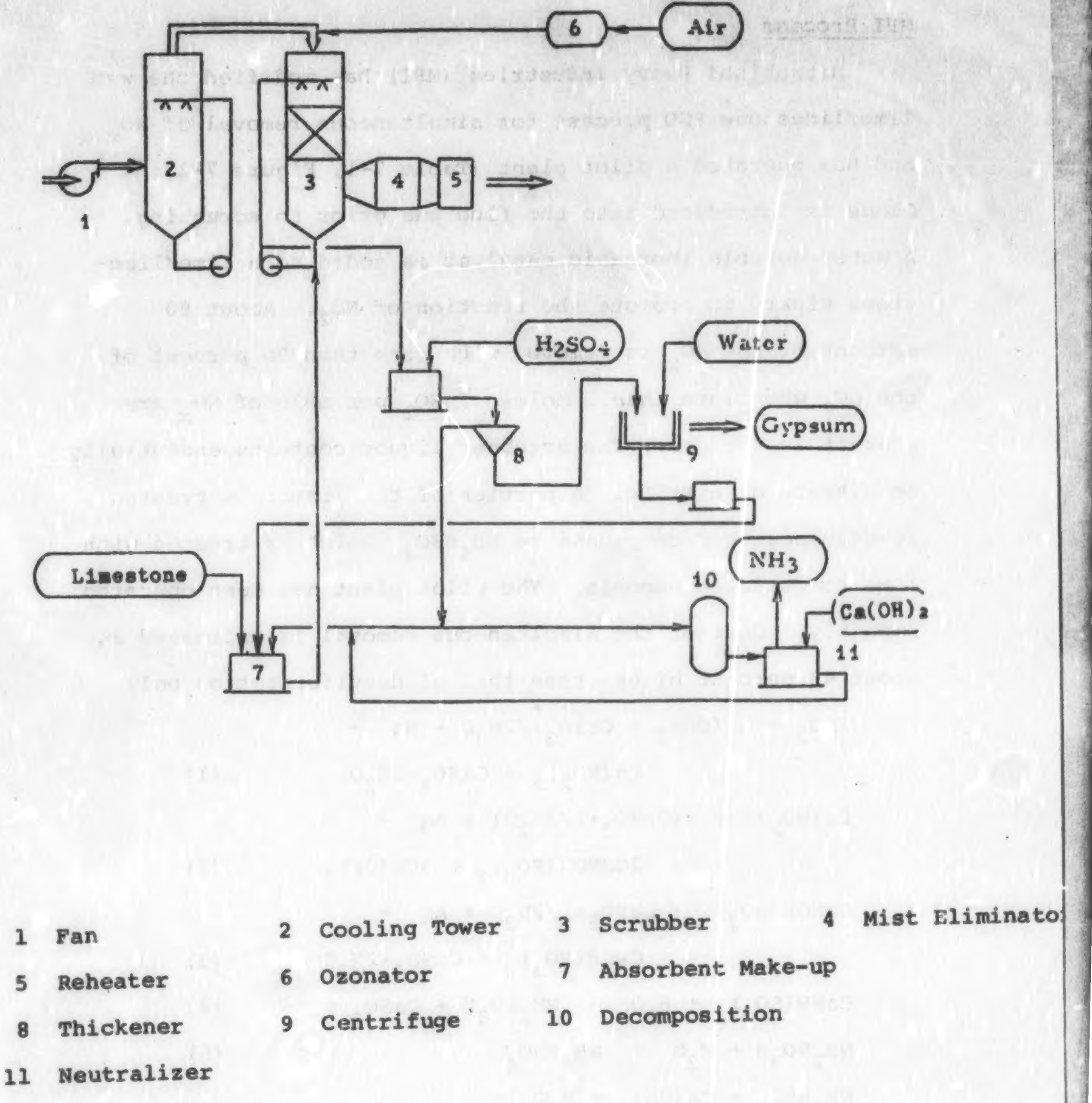

Air
6
1
2
3
4
5
H₂SO₄
Water
Gypsum
8
9
Limestone
NH₃
10
Ca(OH)₂
11
7
1 Fan
2 Cooling Tower
3 Scrubber
4 Mist Eliminato
5 Reheater
6 Ozonator
7 Absorbent Make-up
8 Thickener
9 Centrifuge
10 Decomposition
11 Neutralizer

Figure 7-3. MHI simultaneous removal process.

## MHI Process

Mitsubishi Heavy Industries (MHI) has modified the wet lime/limestone FGD process for simultaneous removal of $NO_x$ and has operated a pilot plant (Table 7-1, Figure 7-3). Ozone is introduced into the flue gas prior to scrubbing. A water-soluble inorganic catalyst is added to a lime/limestone slurry to promote the reaction of $NO_2$. About 80 percent of the $NO_x$ is removed with more than 90 percent of the $SO_2$ when more than 3 moles of $SO_2$ per mole of $NO_x$ are present in the gas. The scrubber liquor contains essentially no nitrate or nitrite. A portion of the liquor is treated to decompose N-S compounds to $NH_4HSO_4$, which is treated with lime to generate ammonia. The pilot plant has been operated smoothly. Cost of the simultaneous removal is estimated at about 40 percent higher than that of desulfurization only.

$$2NO_2 + Ca(OH)_2 + CaSO_3 1/2H_2O + Aq \rightarrow Ca(NO_2)_2 + CaSO_4 \cdot 2H_2O \qquad (1)$$

$$Ca(NO_2)2 + 4(CaSO_3 \cdot 1/2H_2O) + Aq \rightarrow 2CaNOH(SO_3)_2 + 3Ca(OH)_2 \qquad (2)$$

$$CaNOH(SO_3)_2 + CaSO_3 \cdot 1/2H_2O + Aq \rightarrow CaNH(SO_3)_2 + CaSO_4 \cdot 2H_2O \qquad (3)$$

$$CaNH(SO_3)_2 + H_2O \rightarrow NH_2SO_3H + CaSO_4 \qquad (4)$$

$$NH_2SO_3H + H_2O \rightarrow NH_4HSO_4 \qquad (5)$$

$$NH_4HSO_4 + Ca(OH)_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + NH_4OH \qquad (6)$$

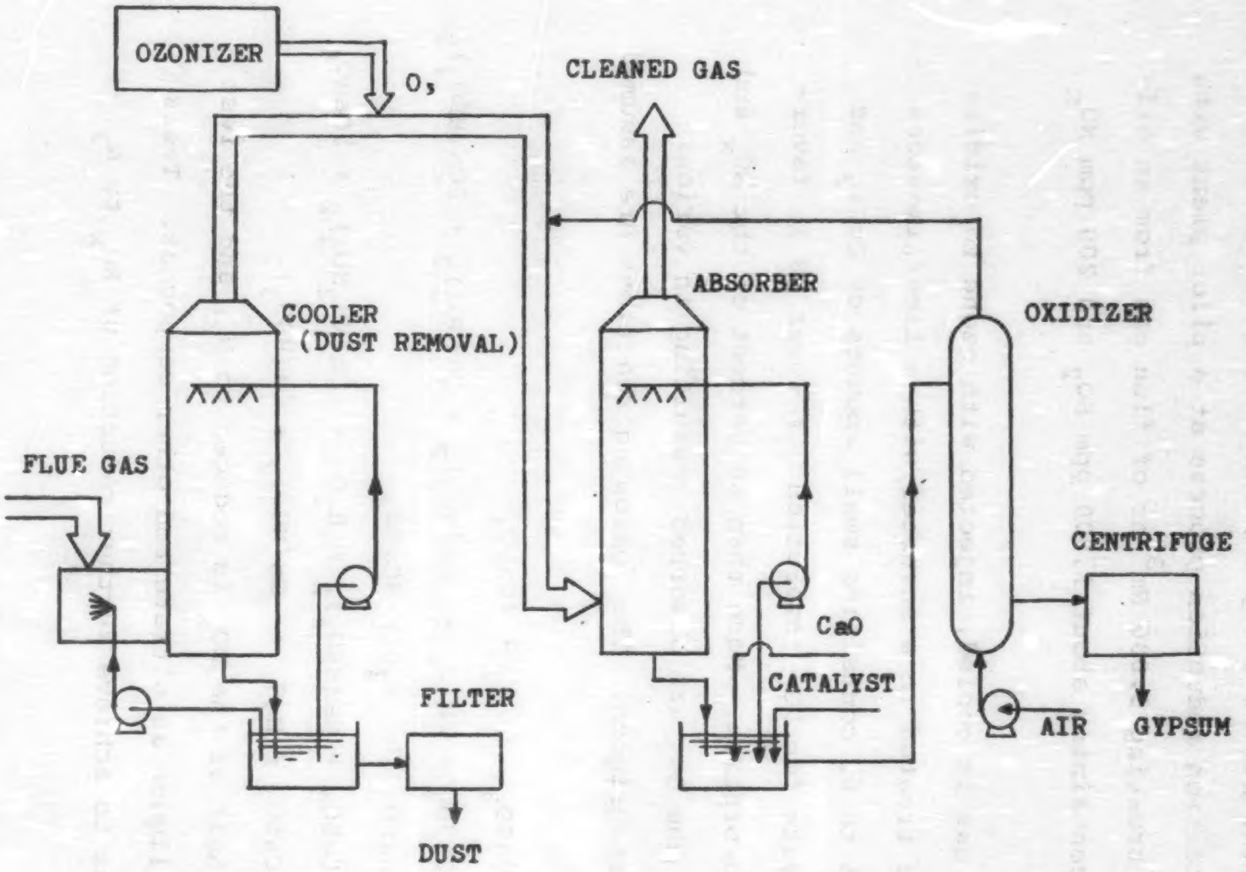

OZONIZER
$O_3$
CLEANED GAS
ABSORBER
COOLER
(DUST REMOVAL)
OXIDIZER
FLUE GAS
CENTRIFUGE
CaO
CATALYST
FILTER
AIR
GYPSUM
DUST

Figure 7-4 Schematic flowsheet of IHI simultaneous removal process

## IHI Process[13]

Ishikawajima-Harima Heavy Industries (IHI) has been testing an oxidation reduction process at a pilot plant with a capacity of treating 5,000 $Nm^3$/hr of flue gas from an oil-fired boiler containing about 1,000 ppm $SO_2$ and 200 ppm $NO_x$ (Figure 7-4).

The flue gas is cooled, injected with ozone to oxidize NO to $NO_2$, and treated in a scrubber with a lime/limestone slurry at pH 5 to 6, containing small amounts of $CuCl_2$ and NaCl as catalysts for $NO_x$ absorption. A lower pH is favorable to $NO_x$ absorption. More than 80 percent of the $NO_x$ and 90 percent of the $SO_2$ are absorbed, resulting in various reactions in the liquor. The following reactions are assumed to take place:

$$2NO_2 + 4CaSO_3 \rightarrow N_2 + 4CaSO_4$$

$$4NO_2 + 4CaSO_3 + 2H_2O \rightarrow Ca(NO_2)_2 + Ca(NO_3)_2 + 2Ca(HSO_3)_2$$

$$2NO_2 + 3CaSO_3 \rightarrow N_2O + 3CaSO_4$$

$$2NO_2 + 5CaSO_3 + Ca(HSO_3)_2 + H_2O \rightarrow Ca(NH_2SO_3)_2 + 5CaSO_4$$

$$N_2O_5 + 2CaSO_3 + H_2O \rightarrow Ca(NO_3)_2 + Ca(HSO_3)_2$$

About a half of the $NO_x$ is reduced to $N_2$, and the rest stays in the liquor as nitrate and other compounds. Tests are in process to achieve further reduction of $NO_x$ to $N_2$.

### Chiyoda Thoroughbred 102 Process

Chiyoda has made a simple modification of the Thoroughbred 101 process to remove $NO_x$. Ozone is added to the gas prior to scrubbing. More than 60 percent of the $NO_x$ is removed along with about 90 percent of the $SO_2$. A portion of the removed $NO_x$ is converted into nitric acid, which forms calcium nitrate, and the rest is converted into $N_2$ and $N_2O$. Wastewater treatment is required to remove the nitrate.

### Other Oxidation-Reduction Processes

Osaka Soda, a chemical company, has developed a process similar to the Fujikasui-Sumitomo process and has constructed a prototype unit (Table 7-1). Tests on wastewater treatment are in progress.

Shirogane Co., an engineering company, has built a unit (Table 7-1) using a process similar to the Fujikasui-Sumitomo process except that ozone is substituted for chloride dioxide. The wastewater containing sodium sulfate and nitrate is sent to a wastewater treatment system along with other wastewaters.

## REDUCTION PROCESSES

### Kureha Process

Kureha Chemical has developed a process to remove $NO_x$ in combination with the sodium acetate FGD process (Section 6) (Figure 7-5).

$SO_2$ is absorbed by a sodium acetate solution to produce sodium sulfite and acetic acid. NO is absorbed by a sodium sulfite solution in the presence of acetic acid and a soluble metallic catalyst to produce sodium imidodisulfonate [reaction (2)].

$$SO_2 + 2CH_3COONa + H_2O \rightarrow Na_2SO_3 + 2CH_3COOH \qquad (1)$$

$$\begin{aligned} &2NO + 5NaSO_3 + 4CH_3COOH \rightarrow 2NH(SO_3Na)_2 \\ &\quad + Na_2SO_4 + 4CH_3COONa + H_2O \qquad (2) \end{aligned}$$

The remaining sodium sulfite is air-oxidized into sulfate. The sulfate is treated with calcium acetate, as in the FGD process.

Sodium imidodisulfonate is reacted with slaked lime to precipitate and separate sodium calcium imidodisulfonate [reaction (3)], which is then hydralized in the presence of sulfuric acid into sulfamic acid [reaction (4)]. The sulfamic acid is treated with calcium nitrite to release nitrogen [reaction (5)].

$$\begin{aligned} &NH(SO_3Na)_2 + Ca(OH)_2 + CH_3COOH \\ &\quad \rightarrow NNa(SO_3)_2Ca + CH_3COONa + 2H_2O \qquad (3) \end{aligned}$$

$$\begin{aligned} &2NNa(SO_3)Ca + H_2SO_4 + 2H_2O \\ &\quad \rightarrow 2NH_2SO_3H + Na_2SO_4 \overset{\downarrow}{+} 2CaSO_4 \qquad (4) \end{aligned}$$

$$\begin{aligned} &2NH_2SO_3H + Ca(NO_2)_2 \\ &\quad \rightarrow 2N_2 + CaSO_4 + H_2SO_4 + 2H_2O \qquad (5) \end{aligned}$$

Kureha has been operating a pilot plant with a capacity of treating 5,000 $Nm^3/hr$ of flue gas from an oil-fired boiler. The process seems fairly complicated, since it includes many reaction steps. Recently the sodium imidodisulfonate has been found useful as a builder of detergents to replace sodium tripolyphosphate, which has been causing eutrophication problems. Tests have been in progress on the effect of the disulfonate on the environment. Possible commercial use of the disulfonate will make the process useful.

## Mitsui Shipbuilding Process[11]

Mitsui Shipbuilding, one of the largest engineering and construction companies, has developed a simultaneous removal process which by-produces concentrated $SO_2$ which can be used in sulfuric acid production (Figure 7-6).

Flue gas is treated with a ferrous compound solution containing ethylenediaminetetraacetate, which absorbs both $SO_2$ and NO.

A portion of the ferrous ion is converted to ferric ion by the oxygen in the flue gas. The absorbed liquor is sent to a reduction step, where the ferric ion is reduced to ferrous ion by electrolysis.

The liquor is then sent to a stripper, where it releases concentrated $SO_2$ and NO by steam distillation. The NO is reduced to $N_2$; the $SO_2$ is used in sulfuric acid production. The liquor from the scrubber is returned to the absorber. In tests with a pilot plant (150 $Nm^3/hr$) about 95% of the $SO_2$ and 85 percent of the $NO_x$ were removed at an L/G ratio of 1 liter/$Nm^3$.

It is estimated that the cost is $80 million for a 67 MW system, EDTA consumption per year is 300 to 400 tons ($500,000 to 600,000), and simultaneous removal cost is $34/kl oil, including fixed costs.

By use of $H_2S$ in the reduction step, elemental sulfur may be produced. Tests with a larger plant are required for further evaluation.

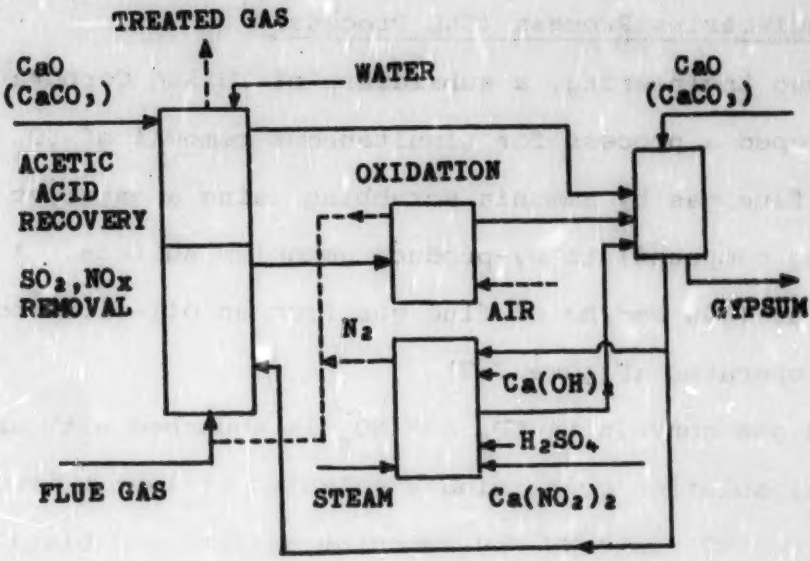

TREATED GAS
CaO
(CaCO$_3$)
WATER
CaO
(CaCO$_3$)
ACETIC
ACID
RECOVERY
OXIDATION
SO$_2$,NO$_x$
REMOVAL
AIR
GYPSUM
N$_2$
Ca(OH)$_2$
H$_2$SO$_4$
FLUE GAS
STEAM
Ca(NO$_2$)$_2$

Figure 7-5 Flowsheet of Kureha simultaneous removal process

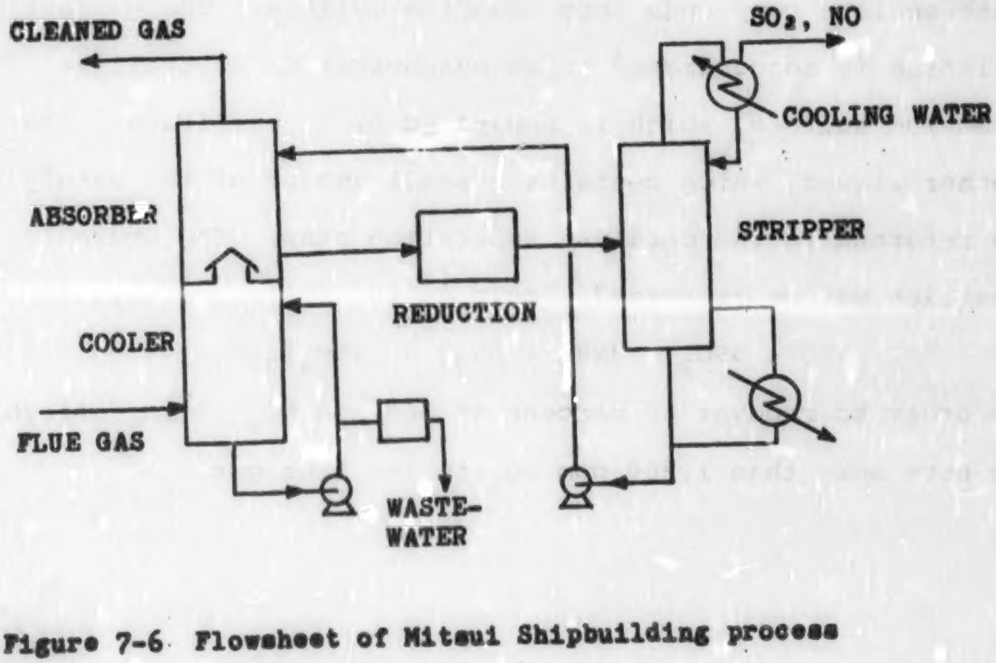

CLEANED GAS
SO$_2$, NO
COOLING WATER
ABSORBER
STRIPPER
REDUCTION
COOLER
FLUE GAS
WASTE-
WATER

Figure 7-6 Flowsheet of Mitsui Shipbuilding process

## Chisso Engineering Process (CEC Process)[11]

Chisso Engineering, a subsidiary of Chisso Corporation, has developed a process for simultaneous removal of $SO_2$ and $NO_x$ from flue gas by ammonia scrubbing using a catalyst (chelating compound) to by-produce ammonium sulfate. A pilot plant (300 $Nm^3$/hr of flue gas from an oil-fired boiler) has been operated (Figure 7-7).

Flue gas containing $SO_2$ and $NO_x$ is absorbed with an ammoniacal solution containing a soluble catalyst to reduce the absorbed $NO_x$ into $NH_3$ by ammonium sulfite and bisulfite, which are formed from $SO_2$ and ammonia. Most of the catalyst is separated from the product solution containing ammonium sulfate and sulfite and intermediate compounds. The solution is oxidized by air and then heated to convert the intermediate compounds into ammonium sulfate. The product solution is concentrated in an evaporator to crystallize ammonium sulfate, which is separated by a centrifuge. The mother liquor, which contains a small amount of the catalyst, is returned to the catalyst separation step. The overall reaction may be expressed simply in the following way:

$$2NO + 5SO_2 + 8NH_3 + 8H_2O = 5(NH_4)_2SO_4$$

In order to recover 80 percent of 300 ppm $NO_x$ it is desirable to have more than 1,200 ppm $SO_2$ in the flue gas.

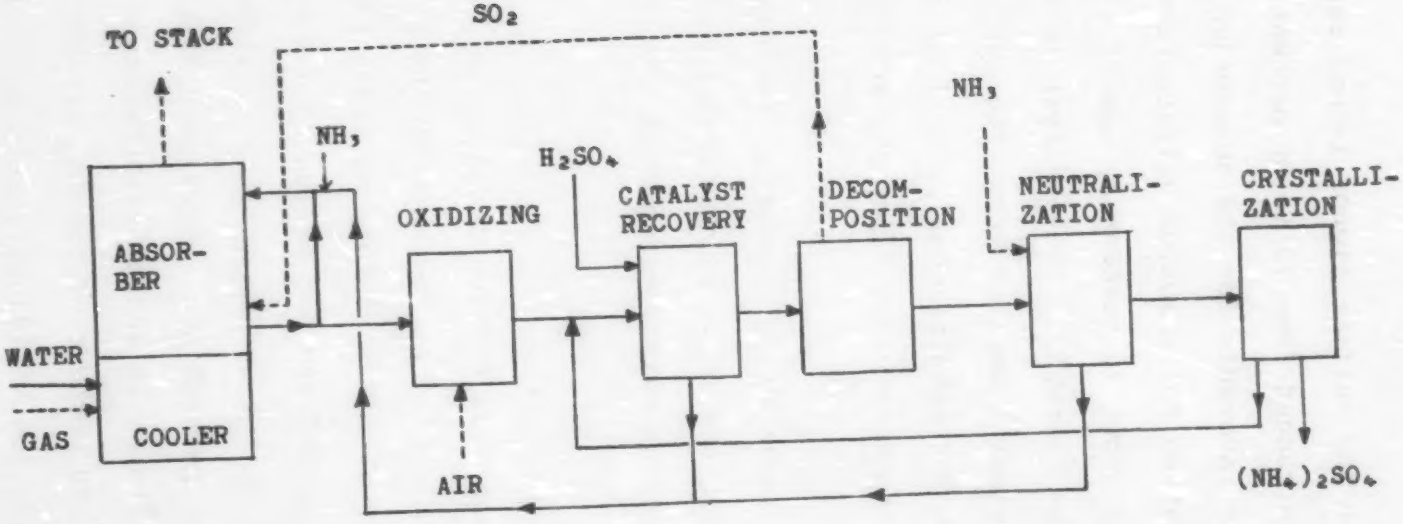

TO STACK
$SO_2$
$NH_3$
$H_2SO_4$
$NH_3$
ABSOR-BER
COOLER
WATER
GAS
OXIDIZING
AIR
CATALYST RECOVERY
DECOM-POSITION
NEUTRALI-ZATION
CRYSTALLI-ZATION
$(NH_4)_2SO_4$

Figure 7-7 Flowsheet of CEC process

Reaction of $NO_x$ with the sulfite liquor is not rapid, and the removal ratio has ranged from 70 to 80 percent. The use of a dilute liquor is favorable for the absorption but necessitates much evaporation for ammonium sulfate recovery. Therefore, $NO_x$ removal of about 70 percent by use of a moderate concentration may be suitable. The catalyst is not affected by nickel and vanadium derived from flue gas. Chisso estimates the cost for simultaneous removal of $SO_2$ and $NO_x$ to be about 40 percent more than for $SO_2$ removal only.

The process has the advantage of producing ammonium sulfate, utilizing both $SO_2$ and $NO_x$. Plume formation common to ammonia scrubbing processes might be a problem for this process.

Asahi Chemical Process

Asahi Chemical Co. has been testing a reduction process with a pilot plant (600 $Nm^3/hr$). A flowsheet of the process is shown in Figure 7-8. A flue gas containing 1,250 ppm $SO_2$, 3 to 4 percent $O_2$, and 200 ppm $NO_x$ is led to a sieve-tray absorber and treated with a sodium sulfite solution at pH 6.3 containing EDTA and ferrous ion. More than 80 percent of the $NO_x$ is absorbed, forming an adduct with ferrous ion and EDTA, while more than 90 percent of the $SO_2$ is absorbed reacting with the sulfite. The NO adduct reacts with the sulfite to form sodium sulfate and nitrogen by the following reaction:

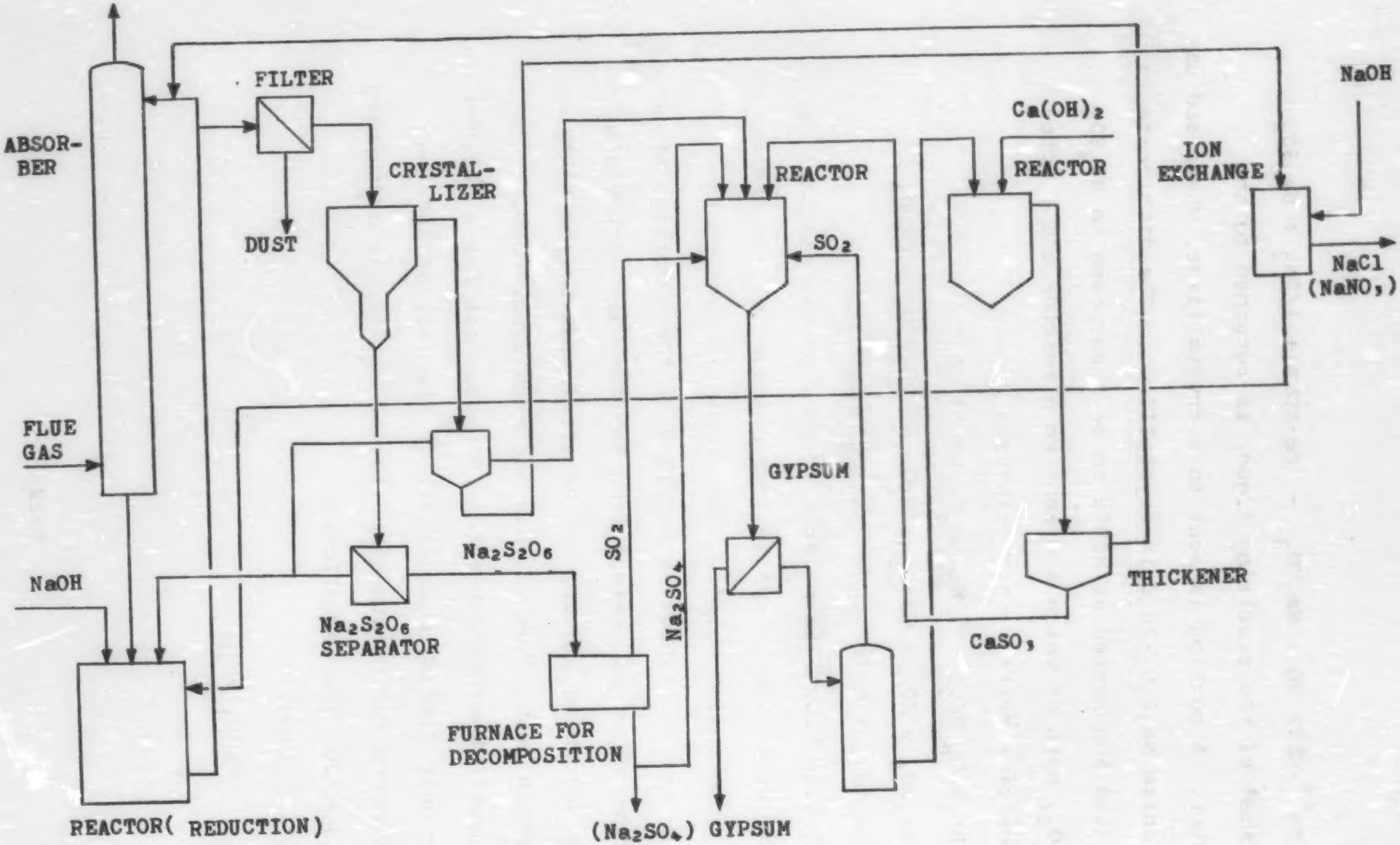

ABSOR-
BER
FILTER
DUST
CRYSTAL-
LIZER
FLUE
GAS
NaOH
REACTOR( REDUCTION)
Na2S2O6
SEPARATOR
Na2S2O6
FURNACE FOR
DECOMPOSITION
SO2
Na2SO4
(Na2SO4) GYPSUM
REACTOR
SO2
GYPSUM
Ca(OH)2
REACTOR
THICKENER
CaSO3
ION
EXCHANGE
NaOH
NaCl
(NaNO3)

Figure 7- 8 Flowsheet of Asahi Chemical reduction process

$Fe^{++}\cdot EDTA\cdot NO + Na_2SO_3 \rightarrow Fe\cdot EDTA + 1/2N_2 + Na_2SO_4$

Most of the resulting liquor is returned to the absorber. A portion is sent to a crystallizer, where sodium dithionate $Na_2S_2O_6\cdot 2H_2O$ is crystallized. The dithionate is separated and heated at 300°C to be decomposed to $Na_2SO_4$ and $SO_2$, both of which are sent to a reactor and reacted with calcium sulfite to precipitate gypsum.

$Na_2S_2O_6\cdot 2H_2O \rightarrow Na_2SO_4 + SO_2 + 2H_2O$

$Na_2SO_4 + SO_2 + CaSO_3 + H_2O \rightarrow 2NaHSO_3 + CaSO_4$

$2N_aHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3$

Sodium bisulfite solution formed by the reaction is treated with lime to precipitate calcium sulfite and to regenerate sodium sulfite; the former is sent to the reactor and the latter is recycled to the absorbing system. Chloride, which is derived from the fuel and accumulates in the scrubbing liquor, can be eliminated by ion exchange, with which Asahi Chemical has had much experience.

Asahi Chemical estimates that the cost for a 500,000 $Nm^3$/hr unit (160 MW equivalent) is $16 million and that requirements for treatment of 10,000 $Nm^3$ of gas containing 2,000 ppm $SO_2$ are as follows:

| | |
|---|---|
| $Ca(OH)_2$ | 6.7 kg |
| $FeSO_4\cdot 7H_2O$ | 1.0 kg |
| EDTA | 1.0 kg |

| | |
|---|---|
| NaOH | 4.2 kg |
| Oil (gas reheating) | 30 kg |
| Oil (thermal decomposition) | 5 kg |
| Steam | 60 kg |
| Cooling water | 6 tons |
| Power | 15 kWh |

The system is not simple but represents a combination of feasible unit processes. Operation data of a larger pilot plant may be needed for a reliable evaluation of commercial feasiblity.

Kawasaki Magnesium Process

Kawasaki Heavy Industries has been operating a pilot plant with magnesium scrubbing with a capacity of treating 5,000 $Nm^3$/hr of flue gas from a coal-fired boiler (Table 7-1, Figure 7-9).

The gas, containing about 1,000 ppm $SO_2$ and 400 ppm $NO_x$, is mixed with $NO_2$ gas to adjust the $NO_2/NO$ ratio to 1 and is treated with a magnesium hydroxide slurry to form magnesium sulfite and nitrite. The nitrite is separated and decomposed by adding sulfuric acid to produce NO, which is oxidized to $NO_2$ and returned to the absorber. The magnesium sulfite is oxidized into sulfate and reacted with calcium nitrate to precipitate gypsum, which is centrifuged. The separated magnesium nitrate solution is reacted with

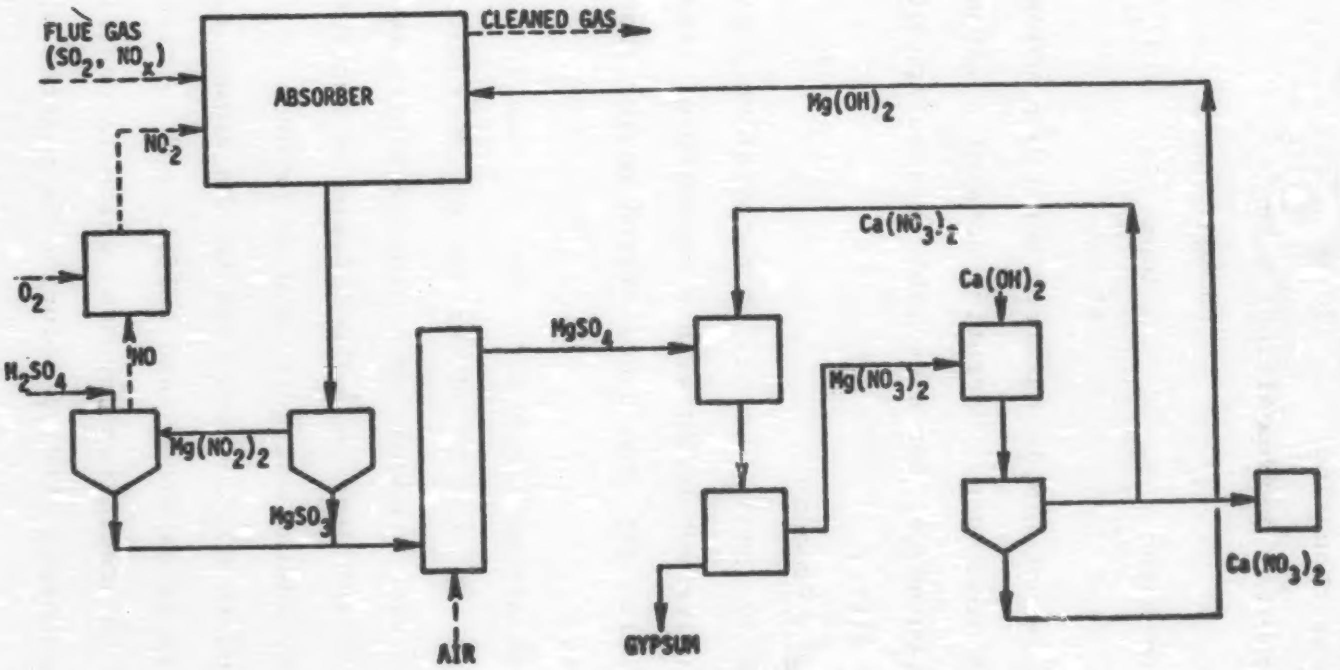

FLUE GAS
($SO_2$, $NO_x$)
CLEANED GAS
ABSORBER
$NO_2$
$Mg(OH)_2$
$O_2$
NO
$H_2SO_4$
$Mg(NO_2)_2$
$MgSO_3$
$MgSO_4$
AIR
GYPSUM
$Ca(NO_3)_2$
$Ca(OH)_2$
$Mg(NO_3)_2$
$Ca(NO_3)_2$

Figure 7-9. Flowsheet of Kawasaki magnesium process.

calcium nitrate to precipitate gypsum, which is centrifuged. The separated magnesium nitrate solution is reacted with calcium hydroxide to precipitate magnesium hydroxide, which is returned to the absorber. Part of the calcium nitrate liquor formed by the reaction is returned to the system for the reaction with magnesium sulfate and the rest is obtained as by-product.

The process has the advantage of removing both $SO_2$ and $NO_x$ while by-producing gypsum and calcium nitrate. The process is not simple, however, and the demand for by-product calcium nitrate is limited.

## DRY PROCESSES FOR SIMULTANEOUS REMOVAL

### Reaction of Activated Carbon

Activated carbon has been used commercially as the absorbent of $SO_2$. Although it also absorbs $NO_x$, the absorbing capacity is not sufficient to treat a large amount of gas. Takeda Chemical has produced an activated carbon containing metallic components or with a special structure to promote the reaction of $NO_x$ with ammonia to form $N_2$. Higher temperature is favorable to the reaction but decreases the $SO_2$ absorbing capacity (Figure 7-10). Optimum temperature for simultaneous removal by this process is about 250°C.

$$2NH_3 + 2NO + 1/2O_2 = 2N_2 + 3H_2O$$

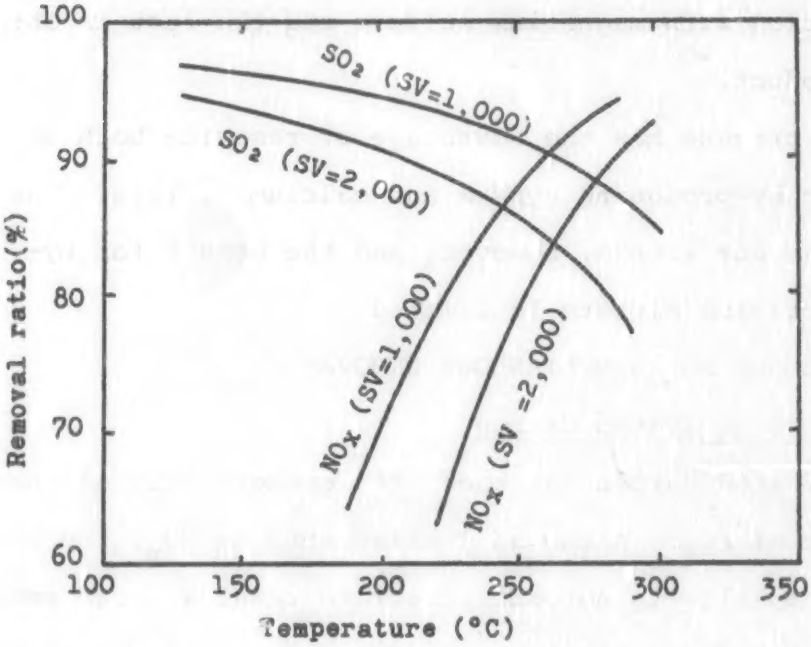


Figure 7-10. Schematic diagram of $SO_2$ and $NO_x$ removal by activated carbon at different temperatures and space velocities.

Carbon for simultaneous removal of $SO_2$ and $NO_x$ costs about 8,000/t, whereas carbon used commercially for FGD costs \$3,000/t. Simultaneous removal for flue gas from a 300 MW boiler will require about 1,000 t of the carbon, which may be too expensive. The price will be substantially lowered through mass production.

## Unitika Activated Carbon Process

Unitika Co. recently started operating a pilot plant with a capacity of treating 4,500 $Nm^3$/hr of flue gas from a glass melting furnace; the gas contains about 400 ppm $SO_2$ and 500 ppm $NO_x$ (Figure 7-11). The plant has a tower with four compartments, all of which have a fixed carbon bed. About 600 ppm $NH_3$ is added to the gas at about 230°C, and the mixed gas is led into three compartments. About 90 percent of the $NO_x$ and $SO_2$ is removed. The carbon that has absorbed $SO_2$ is heated to 350°C in a reducing hot gas to release concentrated $SO_2$ for sulfuric acid production. Ammonium sulfate and sulfite, which tend to form on the carbon, are decomposed to $SO_2$ and $N_2$ in the regeneration step.

Design and operating parameters are as follows:

| | |
|---|---|
| Tower height | 17 m |
| Carbon bed thickness | 1 m |
| Pressure drop | 100 mm $H_2O$ |

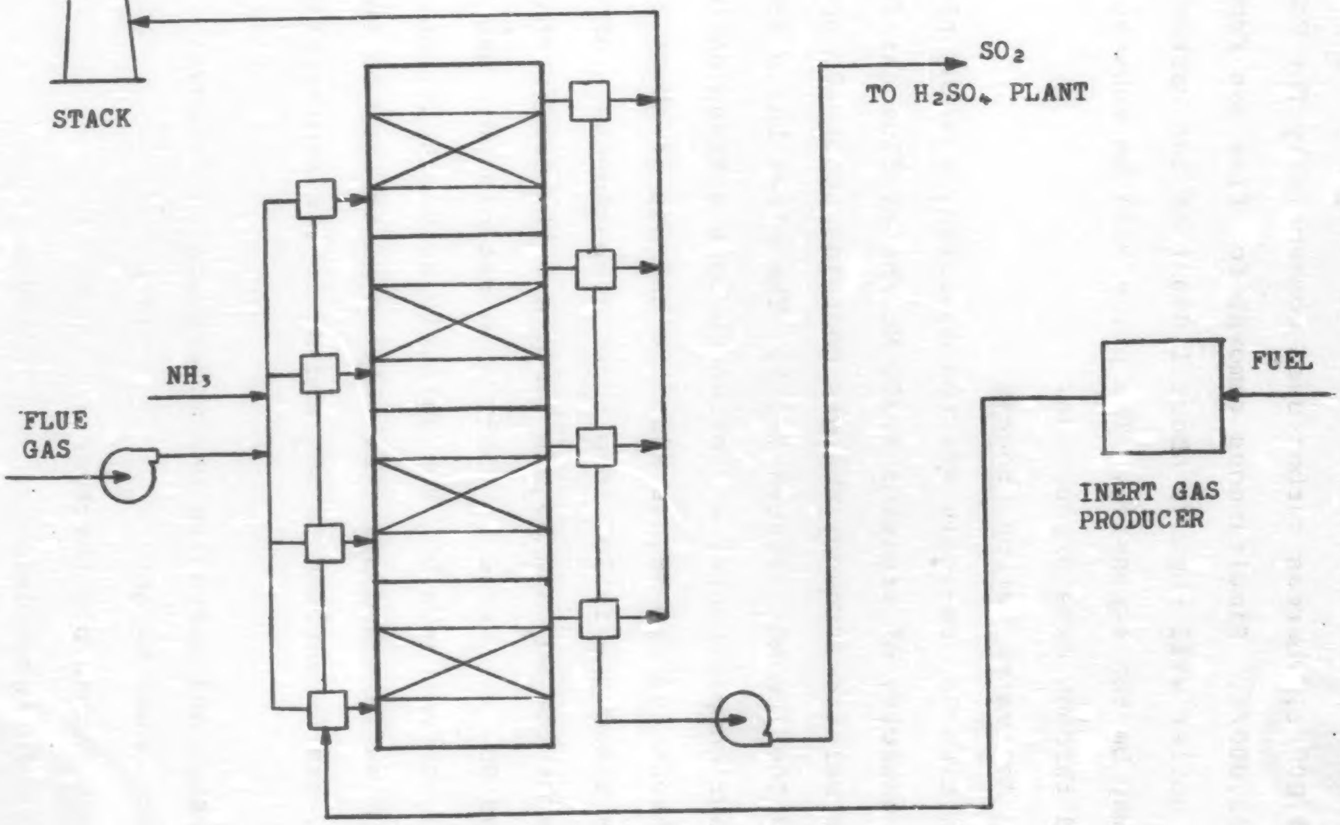

STACK
SO$_2$
TO H$_2$SO$_4$ PLANT
NH$_3$
FLUE GAS
FUEL
INERT GAS PRODUCER

Figure 7-11 Flowsheet of Unitika process

Absorption time for one cycle 3 days

Regeneration time for one cycle 12 hours

$SO_2$ in gas from regeneration step 5-10%

A superficial gas velocity of about 700 is used. The carbon consumption is estimated to be less than 10 percent of a charge per year. In the 6-month operation, the loss has been only 1 to 2 percent. The gas from the regeneration step, containing 5 to 10 percent $SO_2$, may be used for sulfuric acid production.

Other Activated Carbon Processes

Sumitomo Heavy Industries has constructed a prototype FGD system (175,000 $Nm^3$/hr) using moving beds of absorbent activated carbon, which is regenerated by heating a reducing gas.[2] With this unit they have studied simultaneous removal and are constructing a test unit with a capacity of treating 1,500 $Nm^3$/hr flue gas using moving beds.

Hitachi Ltd. has found that activated carbon treated with ammonium bromide is effective even at 100°C for $NO_x$ reduction by ammonia.[14] The low-temperature activity may result in energy saving (Figure 7-1, No. 4), but deposition of ammonium sulfate and bisulfate on the carbon may present a problem.

## Shell Copper Oxide Process

Copper oxide used as an absorbent of $SO_2$ in the Shell process works as catalyst in the reaction of $NO_x$ with ammonia. The Yokkaichi plant, SYS, treating 120,000 $Nm^3$/hr of flue gas from an oil-fired boiler by the Shell process, has introduced ammonia into a reactor at 400°C since 1975. Up to about 70 percent of the $NO_x$ can be removed. Copper sulfate formed by $SO_2$ absorption is reacted with hydrogen to generate concentrated $SO_2$, which is sent to a Claus furnace to produce sulfur.

## Ebara Electron Beam Process[15]

Ebara Manufacturing Co. has developed a unique process for simultaneous removal by electron beam radiation. Flue gas is introduced into a reactor and exposed to the beam. About 80 percent of the $SO_2$ and 90 percent of the $NO_x$ can be removed, forming a sulfuric acid mist and a powdery product containing S, N, O, and H, which are caught by an electrostatic precipitator. A pilot plant (1,000 $Nm^3$/hr) has been operated and a larger plant (3,000 $Nm^3$/hr) is to be constructed. Investment cost and power consumption seem high.

## 8. COMPARATIVE EVALUATION

### DIFFERENCES AFFECTING PROCESS APPLICATIONS IN THE UNITED STATES AND JAPAN

Significant differences in circumstances in the United States and Japan can affect the selection of an FGD process and unit design. The major differences are as follows:

(1) In the United States, gypsum and sulfur from natural sources are plentiful and inexpensive, whereas these are limited in Japan. By-products from desulfurization, including sodium sulfite and gypsum, can be sold in Japan, a fact conducive to the development of recovery processes.

(2) In the United States, most plants have enough space for disposal of waste products, whereas in Japan space limitations necessitate maximum utilization of by-products.

(3) In the United States, about 60 percent of the electric power is generated by burning coal, which gives much fly ash. In Japan, most power plants burn oil, which gives little dust--an advantage in recovering by-products with high purity.

(4) In the United States, many power plants are located far from chemical plants. In Japan, power and chemical plants are usually close to each other; hence it is easy for chemical plants to utilize desulfurization by-products and for power plants to use chemicals.

(5) $SO_2$ concentration of flue gas usually ranges from 400 to 1,500 ppm in Japan, whereas it reaches 2,000 to 3,000 ppm in the United States.

(6) In Japan, many plants are close to cities. More than 90 percent removal of $SO_2$ or less than 100 ppm $SO_2$ in emitted gas is usually required. In the United States, about 85 percent desulfurization or 300 ppm $SO_2$ in the gas is usually acceptable.

(7) Regulations of the purge of wastewater in many states in the United States are more stringent than in Japan.

(8) Compared with flue gas from oil burning, that from coal is richer in $NO_x$ and dust. It is not easy to reduce $NO_x$ concentration in flue gas from coal combustion to less than 400 ppm; moreover, the dust contaminates the catalyst for $NO_x$ removal. Simultaneous removal of $SO_2$ and $NO_x$ by wet processes may be useful for treatment of flue gas from coal combustion.

## WET LIME/LIMESTONE PROCESS

### System Cost and Operation

The plant cost for the Japanese lime/limestone-gypsum process is considerably higher than that for the United States throwaway sludge process because of the requirement of a pH controller (or additional absorber), oxidizer, and centrifuge, which account for about 30 percent of the plant cost. Where there is enough space for sludge discarding, the throwaway process may be most economical.

Most of the lime/limestone-gypsum process systems have a gas cooler before the scrubber, and the scrubber is designed to ensure high $SO_2$ removal efficiency as well as high utilization of the absorbent, both above 95 percent in many cases. These factors make the system more costly but free from serious scaling problems. The gas cooler humidifies the gas and prevents local drying in the scrubber, thus helping to prevent formation of scale. The high $SO_2$ removal and absorbent utilization in the scrubber may reduce scaling of the mist eliminator, as will be discussed below.

Japanese units are usually provided with spare pumps but seldom with a standby scrubber because long-term continuous operation can be carried out without severe scaling problems.

## Saturated or Unsaturated

"Unsaturated mode operation" has been carried out successfully at the Paddy's Run plant, Louisville Power and Electric, and at the Omuta plant, Mitsui Aluminum. The operation prevents gypsum formation by keeping the oxidation of calcium sulfite below 20 percent and thus permits scale-free operation.

Japanese processes producing gypsum are usually operated in the "saturated mode", circulating a slurry containing gypsum as a crystal seed, and might be more widely applicable to various gas compositions. Unsaturated mode operation is not suitable for gases with a low $SO_2/O_2$ ratio such as that from a low-sulfur coal, because the low ratio encourages oxidation. Even with a gas from high-sulfur coal, which normally contains 2,000 to 3,000 ppm $SO_2$ and 4 to 5 percent

$O_2$, there is a possibility of scaling in the scrubber because of gypsum formation due to a temporary increase in the $O_2$ concentration and a temporary decrease in pH of the slurry as the operation load fluctuates.

### Scaling on Mist Eliminator

Scaling tends to occur most readily on mist eliminators where, in addition to wetting and drying, lime or limestone from the mist reacts with $SO_2$. The gas passing through the eliminator usually contains 200 to 400 ppm $SO_2$ and 4 to 5 $O_2$ in the U.S. and 20 to 100 ppm $SO_2$ and 1 to 2 percent $O_2$ in Japan. In both cases gypsum would form by the reaction with lime or limestone because of the low $SO_2/O_2$ ratio. Washing the eliminator with fresh water can dissolve the gypsum but will increase the wastewater load. The scaling may be reduced by washing with a supernatant of gypsum slurry containing fine crystals of gypsum, which can serve as crystal seed, as has been done in Japan.

It has been argued that scale-free operation of wet lime/limestone process systems in Japan may be due largely to the low $SO_2$ concentration of inlet gas, which is below 600 ppm in many units. However, the inlet $SO_2$ concentration may not be very important because new full-scale systems for oil- or coal-fired utility boilers (250-500 MW) with $SO_2$ concentrations of 1,500 to 1,800 ppm in the gas have been in scale-free operation even with frequent changes of operation load. For prevention of scale on the mist eliminator, the $SO_2$ concentration in the scrubber outlet gas and the utilization of lime or limestone in the scrubber may be important. The presence of much unreacted lime or limestone in the mist and much $SO_2$ in the gas flowing through the eliminator would increase formation of gypsum on the eliminator.

In Japan, the outlet $SO_2$ concentration is low because of the stringent regulation, and the utilization of lime or limestone usually exceeds 95 percent or 90 percent because of the necessity to produce high-quality gypsum. Such a situation may have reduced the scaling on the mist eliminator. The high utilization of lime or limestone is obtained by a good gas-liquid contact resulting from suitable scrubber design, by increasing the liquid/gas ratio, and by the fine grinding of limestone in a wet mill to pass 325 mesh. The high utilization of lime and limestone tends to reduce the pH of the slurry, increase the oxidation, and encourage the formation of gypsum.

Many of the Japanese companies once used a zigzag baffle-type mist eliminator placed horizontally at the top of the scrubber, such as is widely used in the United States, because it is relatively inexpensive; now they seldom use this type because performance is poor. Many now place the mist eliminator vertically in a separate vessel in the exit duct outside the scrubber because this configuration provides better drainage and better over-all performance.

## Effect on Fly Ash and Wastewater on Scaling

The effect of fly ash on scaling is not yet clear. The ash from coal consists of fine, spherical, glassy particles having little reactivity. The ash would increase erosion when present in large amounts in the slurry but not always increase scaling. It might help prevent scaling because of its nonreactive, erosive nature, as pointed out by R.H. Borgwardt, EPA. At present, six FGD systems for coal-fired utility boilers (160 to 300 MW) are in operation in Japan. One of them uses the unsaturated mode and the others use the saturated mode. Operation of all six plants is virtually trouble-free. They are equipped with electrostatic precipitators which remove most of the fly ash, and thus the effect of fly ash has not been clearly demonstrated.

It has been stated that Japanese FGD units purge wastewater to add large amounts of fresh water to the system and thus help to reduce scaling.[1] This view may not be correct, because the sum of wastewater and moisture in the by-product gypsum is no larger than in the United States practice, where the sludge normally contains 60 percent or more water. As shown in Table 3-8, the water ratio or the equivalent water ranges from 26 to 64 percent for the plants using wet lime/limestone processes.

## INDIRECT LIME/LIMESTONE PROCESS

### Sodium Scrubbing

In the United States the sodium scrubbing double alkali processes are simple, as they use lime and by-produce calcium sulfite sludge; in Japan the processes are fairly complex, as they use limestone and are equipped with sulfate decomposition and gypsum recovery units. Limestone is cheaper than lime but limestone processes require larger reactors.

In both processes a portion of the sodium sulfite is oxidized to form sulfate ion, which must be removed from the system. In the U.S. systems, sulfate ion is removed in two ways: (1) by entering calcium sulfite crystals replacing sulfite ion and (2) as sodium sulfate solution contained in the sludge. The oxidation of the sulfite must be maintained under a certain level to prevent accumulation of sodium sulfate in the liquor. The process suits high-sulfur coal but may not suit low-sulfur coal, because it needs a flue gas with a relatively high $SO_2/O_2$ ratio.

The Japanese processes, Kureha-Kawasaki and Showa Denko, incorporate a sulfate decomposition unit. This makes them costly, but they are applicable to any kind of gas.

Gypsum grows into much larger crystals than does calcium sulfite and is washed well. Sodium content in the by-product gypsum is less than 0.1 percent, whereas in the U.S. systems the content in the sulfite sludge usually exceeds 2 percent.

## Other Indirect Processes

The Chiyoda and Dowa processes are much simpler than the above-mentioned Japanese processes. Compared with the U.S. systems, they are more complex because of the requirement for an oxidizer; moreover, they need higher L/G ratios because of the low pH of the absorbing liquor. They do, however, offer the following advantages: (1) use of limestone, (2) much smaller sizes of thickener and filter, (3) smaller loss of absorbent, (4) less possibility of scaling, and (5) applicability to any kind of gas, including that from low-sulfur coal. They may be most applicable at plants that do not require very high $SO_2$ removal efficiency.

The Kurabo ammonium sulfate and Kureha sodium acetate processes use lime, as do the U.S. processes. Although they are less simple than the U.S. processes, they provide some advantages. The Kurabo process gives virtually no plume, which has been a common problem for ammonia scrubbing processes. The Kureha process can recover more than 99 percent of the $SO_2$. Although such a high removal ratio is not usually needed, in certain districts it may be a good idea to treat 70 to 80 percent of flue gas by this process and then mix the treated gas with untreated hot gas to eliminate reheating.

## OTHER PROCESSES (RECOVERY PROCESSES)

Four types of FGD processes are in commercial use in Japan to by-produce concentrated $SO_2$, which is used to produce sulfuric acid or is sent to a Claus furnace to produce elemental sulfur. These are the Wellman-Lord, magnesium (or zinc) scrubbing, activated carbon, and the Shell processes.

The Wellman-Lord process has been most widely used because of smooth operation of the systems and recovery of virtually all of the $SO_2$, which permits substantial reduction of the size of the sulfuric acid plant relative to a conventional plant using 7 to 9 percent $SO_2$ gas obtained by burning pyrite or sulfur. The process, however, is becoming increasingly costly as regulations concerning wastewater become increasingly stringent.

The magnesium scrubbing process has the advantage of giving virtually no wastewater. But operation of a rotary kiln may not be willingly accepted by power companies. The recovered $SO_2$, having a low concentration of 7 to 8 percent, can be used in producing sulfuric acid or in charging into a Claus furnace; it is not suitable for reduction to $H_2S$ to produce elemental sulfur. It may be said that magnesium scrubbing better suits chemical plants and oil refineries, and the Wellman-Lord process better suits power plants.

Carbon absorption with thermal regeneration gives a moderate concentration of the recovered $SO_2$ (about 20 percent) which can be used for production of both sulfuric acid and sulfur. Consumption of carbon increases when a moving bed is used and makes the process costly, particularly in Japan where good-quality and expensive (about $2,700/t) carbon is used. Cheaper carbon is useful but has a lower absorbing capacity and tends to burn during the operation.

The carbon process using a fixed bed and water wash has proved to consume very little carbon. Although the by-produced sulfuric acid is weak, it can be concentrated to about 60 percent by the heat of flue gas, as has been done by Unitika. The process may be suitable for certain chemical plants that can use the acid.

The Shell process seems more costly than the other recovery processes because hydrogen is needed for regeneration. The process is advantageous in that it can effect simultaneous removal of $NO_x$ up to about 70 percent.

## BY-PRODUCT AND WASTEWATER

### Gypsum and Calcium Sulfite

Oversupply of gypsum has presented a problem in Japan where land for disposal is scarce. Because per capita consumption of gypsum in Japan is still about half of that in the United States, a considerable increase in future demand for construction material is expected. Some oversupply may continue, however. Gypsum is not suitable for land filling of ground to support large buildings because it has a little water solubility. A stabilized calcium sulfite sludge, which has been produced in the United States, may be better for land filling. Because fly ash is scarce in Japan, industrial slags may be used instead.

In contrast with current practice, gypsum may be produced in the future in certain districts in the United States. Gypsum by-produced from desulfurization of flue gas from coal has proved useful for cement and wallboard production, as recently practiced in Japan. It may be possible to substitute the gypsum for a portion of that now imported to the United States which amounts to 7 million tons yearly. Gypsum can be piled up to heights of more than 100 feet, as is done at phosphoric acid plants in Florida, thus allowing a great saving of land space as compared with the use of calcium sulfite sludge ponds.

## Elemental Sulfur

Generally speaking, less effort has been made in Japan than in the United States to develop FGD processes that yield elemental sulfur as a by-product. Several oil refineries have installed FGD units to recover concentrated $SO_2$, which is sent to an existing Claus furnace to recover sulfur. Ammonia scrubbing with the IFP reactor to by-produce sulfur has been tested by Mitsubishi Heavy Industries and Toyo Engineering; this effort will be abandoned, however, because of operational problems including the sulfate decomposition step. Except for these, active research to develop new processes has not been made.

This may be due largely to the use of oil as the major fuel in Japan. Elemental sulfur can be recovered from oil at lower cost by hydrodesulfurization than by FGD. An economical process to by-produce sulfur is being sought, however, for the following two reasons: (1) all other by-products of FGD are in oversupply, and (2) heavy oil suitable for hydrodesulfurization to reduce sulfur below 0.5 percent is limited by the content of metallic impurities that poison the catalyst.

## Chloride and Wastewater

When no wastewater purge is allowed, chloride in the flue gas accumulates in the scrubber liquor and tends to increase corrosion and decrease $SO_2$ removal efficiency. In the throwaway sludge process, the chloride concentration in the liquor may be kept within an acceptable level because a considerable amount of water is removed from the system with the sludge, which normally contains more than 60 percent water. In a process by-producing gypsum, which normally contains less than 10 percent moisture, chloride concentration in the liquor will exceed 5 percent when the coal burned is relatively rich in chloride. Plant cost will be increased by the need for highly corrosion-resistant material, such as in the Kobe Steel calcium chloride process.

Chloride may be removed in a prescrubber by water wash of the gas; the liquor from the prescrubber may be neutralized with lime or limestone, and the resulting sludge may be discarded. In a sodium scrubbing process, a portion of the scrubber liquor may be concentrated to crystallize and separate sodium chloride. All such treatments add considerably to the cost of the process. The author believes that regulations should permit purging of a limited amount of wastewater after treating it thoroughly to remove any impurities that may be harmful to the environment.

## SIMULTANEOUS REMOVAL OF $SO_x$ AND $NO_x$

The present denitrification efforts in Japan have been motivated by the quite stringent regulation. $NO_x$ concentrations in large cities in the United States, such as Los Angeles and Chicago, are much higher than those in Tokyo, Osaka, and other Japanese cities. Although a larger portion of $NO_x$ in crowded cities is derived from automobiles,

$NO_x$ from coal-fired boilers will become significant as consumption of coal increases, because the flue gas is relatively rich in $NO_x$ (from 500 ppm to 1,000 ppm) and it is not easy to reduce the concentration below 400 ppm by combustion control.

Among the denitrification processes, the Exxon process injecting ammonia into flue gas at about 800°C without catalyst would require the least cost. The process has a narrow range of optimum reaction temperatures, and for large-scale applications about 50 percent $NO_x$ removal is expected. Catalytic reduction processes using ammonia can attain over 90 percent removal but entail the problem of catalyst contamination by dust in the gas. The activated carbon process can remove about 90 percent of the $SO_2$ and $NO_x$ simultaneously but requires a large amount of carbon and also involves a dust problem. The Shell process can remove about 70 percent of the $NO_x$ together with about 90 percent of the $SO_2$ with a smaller dust problem due to the use of the parallel passage reactor. Selection of a process should be decided according to the $NO_x$ removal ratio required.

The dry processes using ammonia entail some common problems: (1) Formation of ammonium bisulfate in the gas, which condenses anywhere at lower temperature, for example, in heat exchangers. (2) Possibility of secondary pollution by emission of ammonia, which may occur to a considerable extent when the operation load fluctuates. (3) Widespread use of the ammonia processes on a large scale could cause a worldwide shortage of nitrogen fertilizer.

For these reasons, it is desired to develop not only ammonia-using processes but also wet processes for simultaneous control. The wet process by-producing ammonia or ammonium sulfate is desirable from the standpoint of fertilizer supply and will possibly be used extensively in the future if the process economy can be substantially improved. For plants where the transportation of ammonia or ammonium sulfate may be inconvenient, a combination of the Exxon process with a wet process by-producing ammonia might be useful. The by-produced ammonia may be returned to the boiler to reduce a portion of the $NO_x$ to $N_2$ and thus promote simultaneous removal, for which a low $NO_x/SO_2$ ratio is favorable.

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The process descriptions in this report are based primarily on Ando's visits to the desulfurization plants, his discussions with the users and developers of each process, and data made available by them. In addition, the following publications were used and are cited as references.

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